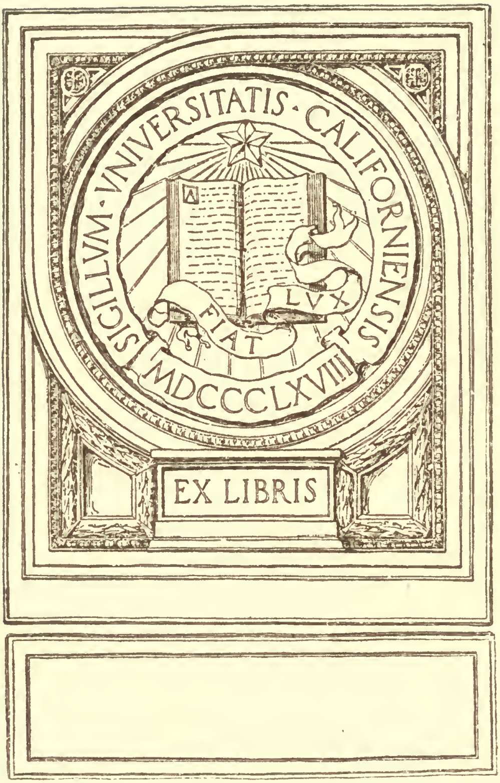

ELEMENTS

OF

INORGANIC CHEMISTRY,

INCLUDING THE

APPLICATIONS OF THE SCIENCE IN THE ARTS.

BY

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AND

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SECOND AMERICAN,

FROM THE SECOND REVISED AND ENLARGED LONDON EDITION.

COMPLETE IN ONE VOLUME.

WITH TWO HUNDRED AND THIRTY-THREE ILLUSTRATIONS ON WOOD.

QUE PROSUNT OMNIBUS.

PHILADELPHIA:
HENRY C. LEA.
1866.

COLLINS, PRINTER

AMERICAN PUBLISHERS' NOTICE.

The publishers have much pleasure in at length presenting Mr. Graham's Inorganic Chemistry complete. The first portion (up to p. 430), was edited in 1852 by Dr. Bridges; the remainder is reproduced without alteration from the English edition, issued a few months since, under the supervision of the Author, by Mr. Watts, whose elaborate Supplement will be found to bring the subjects embraced in the first portion, on a level with the most advanced condition of the science.

The Organic portion of the work, issued in 1843, has not been reproduced by Mr. Graham, nor does he, in his "Advertisement," hold out any promise of its revision and reappearance. The present volume, therefore, contains all that the Author has seen fit to reproduce, being the whole of the two volumes of the London edition.

References have been introduced throughout the first part, to Articles in the Supplement which modify or extend the remarks in the text.

Philadelphia, *April*, 1858.

ADVERTISEMENT.*

The present Volume completes the Work as a Treatise upon Inorganic Chemistry; and it is, accordingly, furnished with an Index of Contents, which applies to both volumes.

From the time which has elapsed since the first publication of these Elements, an amount of alteration and addition had become necessary for properly completing a new edition, which precluded the Author, with his present engagements, from undertaking the task. In these circumstances, he gladly availed himself of the assistance of Mr. Watts, who has supplied a large amount of new matter, including the Supplement, and has edited the volume throughout in the most careful and conscientious manner. The most conspicuous changes now made, by which the work is improved, are the following:—

1. The systematic introduction of the best processes for the separation and quantitative estimation of metals and other important substances, in addition to the description of their properties and reactions. The new methods of *volumetric analysis* are detailed, with the description and applications in particular of Bunsen's General Method.

2. In the Supplement, in which the subjects treated in the first volume are resumed and brought down to the present time: The determination of the most important Physical constants,

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* The observations in this "Advertisement" apply to the second volume of the London edition, which forms p. 431 to end of the present volume.

viz., the Mechanical Equivalent of Heat; the relations between the Chemical and Magnetic effects of the Electric Current, and the reduction of its force to Absolute Mechanical Measure; also the Measurement of the Chemical Action of Light. The Polarization of Light is treated in sufficient detail for the wants of the Chemical Student, attention being especially directed to the methods of Optical Saccharimetry, and to the very remarkable relations between Crystalline Form and Molecular Rotatory Power discovered by Pasteur.

3. The modern views of the constitution and classification of Chemical Compounds are explained at considerable length, chiefly according to Gerhardt's Unitary System. This includes the classification of Organic as well as Inorganic Compounds, as indeed every general system of classification must do. In the same portion of the work, the formation and reactions of the principal classes of organic compounds are explained, so far as appeared necessary to the general understanding of their mutual relations.

4. The last portion of the Supplement contains the most recently discovered facts relating to the Non-metallic Elements, and the Metals of the Alkalies and Earths, a prominent place being assigned to the allotropic modifications of certain elements; viz., Boron, Silicon, Sulphur, Selenium, and Phosphorus, and to the methods of obtaining the alkali and earth-metals in the free state.

THOMAS GRAHAM.

Royal Mint: *December*, 1857.

PREFACE

TO THE SECOND EDITION.

(PART I.)

If the Inorganic department of chemistry has not recently been expanded in the same vast proportion as the Organic branch of the science, still the former has been far from stationary of late years. The advance observed is partly in the old direction of enlarging the list of elements, partly and more conspicuously in supplying deficient members to familiar series of compounds, and in thus enlarging these series,—as in the compounds of chlorine with oxygen, and of sulphur with oxygen. But the most important feature in the recent progress of Inorganic Chemistry has been the rigorous verification which numerical data of all kinds have received, whether relating to physical laws, such as the specific heat of substances, or to chemical properties and composition. The statement of properties and relations has thus acquired a fulness and precision for many substances, which contrasts strongly with the history that could be offered of the same substances even but a very few years ago. The correction and revision of every minute branch of the science was never, indeed, more general and rapid than at the present time. The enlarged means of practical instruction in chemistry, now everywhere provided for the student, and the consequent increase in the number of able investigators, have no doubt contributed much to this result.

Progress of this description cannot fail to affect the theoretical views of chemists, and to promote sound conclusions by affording an extended and safe foundation for reasoning, in a body of well-established facts. It must be admitted that the fundamental views respecting the constitution of salts are at present in a state of transition, but the great questions of chemical theory, if not yet solved, have at least been correctly enunciated, and a general assent obtained to the facts upon which they rest.

In preparing a new edition of his Elements of Chemistry, the Author has incorporated much new and accurate information with the old, while he has endeavoured to give to both the space and the measure of importance which their true value demanded. In such a work, judicious selection of matter is as necessary as careful condensation, while the grounds of the selection are changed with the shifting point of view from which, in a progressive science, the retrospect is taken.

The important bearings of the laws of Heat, particularly in reference to the physical condition of matter, have led to their consideration before the chemical properties of substances, in this as in most other elementary treatises on chemistry. Light is then shortly considered, chiefly in reference to its chemical relations. The principles of its Nomenclature, in which, compared with many sciences, chemistry has been highly fortunate, are then explained, together with the symbolical notation and chemical formulæ in use, by means of which the composition of highly compound bodies is expressed with the same palpable distinctness which, in arithmetic, attends the use of figures, in the place of words, for the expression of numerical sums.

A considerable section of the present volume is then devoted to the consideration of the fundamental doctrines of chemistry, under the heads of combining proportions, atomic theory, doctrine of volumes, isomorphism, isomerism, constitution of salts, chemical affinity and polarity, including the propagation of affinity through metallic and saline media, in the voltaic circle, with the new subject of the atomic volume of solids.

The materials of the inorganic world are then described under two great divisions of non-metallic elements and their compounds, and metallic elements and their compounds.

University College, London,
September, 1850.

PREFACE

TO THE

SECOND AMERICAN EDITION.

(PART I.)

THE "Elements of Chemistry," of which a second edition is now presented, attained, on its first appearance, an immediate and deserved reputation. The copious selection of facts from all reliable sources, and their judicious arrangement, render it a safe guide for the beginner, while the clear exposition of theoretical points, and frequent references to special treatises, make it a valuable assistant for the more advanced student.

From this high character the present edition will in no way detract. The great changes which the science of Chemistry has undergone during the interval, have rendered necessary a complete revision of the work, and this has been most thoroughly accomplished by the author. Many portions will therefore be found essentially altered, thereby increasing greatly the size of the work, while the series of illustrations has been entirely changed in style, and nearly doubled in number.

Under these circumstances but little has been left for the editor. Owing, however, to the appearance of the London edition in parts, some years have elapsed since the first portions were published, and he has therefore found occasion to introduce the more recent investigations and discoveries in some subjects, as well as to correct such inaccuracies or misprints as had escaped the author's attention, and to make a few additional references. Such matter as he has thus introduced has been enclosed in brackets, with his initials appended.

PHILADELPHIA, *March*, 1852.

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CHAPTER I.

HEAT.

The objects of the material world are altered in their properties by heat in a very remarkable manner. The conversion of ice into water, and of water into vapour, by the application of heat, affords a familiar illustration of the effects of this agent in changing the condition of bodies. All other material substances are equally under its influence; and it gives rise to numerous and varied phenomena, demanding the attention of the chemical inquirer.

Heat is very readily communicated from one body to another; so that when hot and cold bodies are placed near each other, they speedily attain the same temperature. The obvious transference of heat in such circumstances impresses the idea that it possesses a substantial existence, and is not merely a quality of bodies, like colour or weight; and when thus considered as a material substance, it has received the name *caloric*. It would be injudicious, however, to enter at present into any speculation on the nature of heat; it is sufficient to remark that it differs from matter, as usually conceived, in several respects. Our knowledge of heat is limited to the different effects which it produces upon bodies, and the mode of its transmission; and these subjects may be considered without reference to any theory of the nature of this agent.

The subject of Heat will be treated of under the following heads:—

1. Expansion, the most general effect of heat, and the Thermometer.
2. Specific heat.
3. The communication of heat by Conduction and Radiation.
4. Liquefaction, as an effect of heat.
5. Vaporization, or the gaseous state, as an effect of heat.
6. Speculative notions respecting the nature of heat.

EXPANSION AND THE THERMOMETER.

All bodies in nature, solids, liquids, or gases, suffer a temporary increase of dimension when heated, and contract again into their original volume on cooling.

1. *Expansion of solids.**—The expansion of solid bodies, such as the metals, is by no means considerable, but may readily be made sensible. A bar of iron which fits easily when cold into a gauge, will be found, on heating it to redness, to have increased sensibly both in length and thickness. The expansion and contraction of metals, indeed, and the immense force with which these changes take place, are matters of familiar observation, and are often made available in the arts. The iron hoops of carriage wheels, for instance, are applied to the frame while they are red hot, and in a state of expansion, and being then suddenly cooled by dashing water upon them, they contract, and bind the wood-work of the wheel with great force. The expansion of solids, however, is very small, and requires nice measurement to ascertain its amount. The expansion in length only has generally been

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* [*See Supplement,* p. 637.]

determined, but it must always be remembered that the body expands also in its other dimensions in an equal proportion. The first general fact observable is, that the amount of dilatation by heat is different in different bodies. No two solids expand alike. The metals expand most, and their rates of expansion are best known. Rods of the undermentioned substances, on being heated from the freezing to the boiling point of water, elongate as follows : —

Zinc (cast)	1 on 323	Pure Gold	1 on 682
Zinc (sheet)	1 " 340	Iron Wire	1 " 812
Lead	1 " 351	Palladium	1 " 1000
Tin	1 " 516	Glass without lead	1 " 1142
Silver	1 " 524	Platinum	1 " 1167
Copper	1 " 581	Flint Glass	1 " 1248
Brass	1 " 584	Black Marble (Lucullite)	1 " 2833

This is the increase which these bodies sustain in length. Their increase in general bulk is about three times greater. Thus, if glass elongates 1 part in 1248 from the freezing to the boiling point of water, it will dilate in cubic capacity 3 parts in 1248, or 1 part in 416. The expanded bodies return to their original dimensions on cooling. Wood does not expand much in length; hence it is occasionally used as a pendulum rod. For the same reason a slip of marble, of the variety mentioned in the preceding table, was employed for that purpose, in constructing the clock of the Royal Society of Edinburgh. Glass without lead expands by the table $\frac{1}{1142}$ part, while the metal platinum expands very little less, $\frac{1}{1167}$. Hence the possibility of cementing glass and platinum together, as is done in many chemical instruments. Other metals pushed through the glass when it is red hot and soft, shrink afterwards so much more than glass on cooling, as to separate from it, and become loose. Zinc is the most expansible of the metals; it expands nearly four times more than platinum from the same heat. But ice, of which the contraction by cold has been observed for 30 or 40 degrees under the freezing point, proves to be more dilatable even than the metals, the rate of this solid being in the proportion of $\frac{1}{267}$th part, while that of zinc is $\frac{1}{323}$d part only. (Brunner (fils), Ann. de Chim. et de Phys., 3 sér. t. 14, p. 377.)

The most important discovery, in a theoretical point of view, that has been made on the subject of the dilatation of solids by heat, is the observation of Professor Mitscherlich, of Berlin, that the angles of some crystals are affected by changes of temperature. This proves that some solids in the crystalline form do not expand uniformly, but more in one direction than in another. Indeed, Mitscherlich has shown that while a crystal is expanding in length by heat, it may actually be contracting at the same time in another dimension. An angle of rhomboidal calcareous spar alters eight and a half minutes of a degree between the freezing and boiling points of water. But this unequal expansion does not occur in crystals of which all the sides and angles are alike, as the cube, the regular octohedron, the rhomboidal dodecahedron. In investigating the laws of expansion among solids, it is advisable, therefore, to make choice of crystallized bodies. For, in a substance not regularly crystallized, the expansion of different specimens may not be precisely the same, as the internal structure may be different. Hence the expansions of the same substance, as given by different experimenters, do not always exactly correspond. The same glass has been observed to dilate more when in the form of a solid rod, than in that of a tube; and the numerous experiments on uncrystallized bodies, which we possess, have afforded no ground for general deductions.

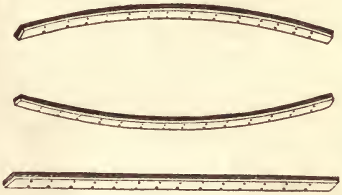
It has been further observed, that the same solid is more expansible at high than at low temperatures, although the increase in the rate of expansion is in general not considerable. Thus, if we mark the progress of the dilatation of a bar of iron under a graduated heat, we find that the increase in dimension is greater for one degree of heat near the boiling point of water, than for one degree near its freezing point. Solids are observed to expand at an accelerated rate, in particular, when heated up to near their fusing points. The cohesion or attraction which subsists between the particles of a solid is supposed to resist the expansive power of heat. But many solids become less tenacious, or soften before melting, which may account for their increasing expansibility. Platinum is the most uniform in its expansions of the metals.

Such changes in bulk, from variations in temperature, take place with irresistible force. This is well illustrated in an experiment, which was first made upon a gallery in the Museum of Arts and Manufactures in Paris, in order to preserve it, and has been successfully repeated in many other buildings. The opposite walls of the edifice referred to were bulging outwards, from the pressure of the floors and roof, which endangered its stability. By the directions of an ingenious mechanic, stout iron rods were laid across the building, with their extremities projecting through the opposite walls so as to bind them together. Half the number of the rods were then strongly heated by means of lamps, and, when in an expanded condition, a disc on either extremity of each rod was screwed firmly up against the external surface of the wall. On afterwards allowing the rods to cool, they contracted, and drew the walls to which they were attached somewhat nearer together. The process was several times repeated, till the walls were restored to a perpendicular position.

The force of expansion always requires to be attended to in the arts, when iron is combined in any structure with less expansible materials. The cope-stones of walls are sometimes held together with clamps, or bars of iron: such bars, if of cast iron, which is brittle, often break on the first frost, from a tendency to contract more than the stone will permit; if of malleable iron, they generally crush the stone, and loosen themselves in their sockets. When cast iron pipes are employed to conduct hot air or steam through a factory, they are never allowed to abut against a wall or an obstacle which they might in expanding overturn. Lead, from its extreme softness, is permanently expanded when repeatedly heated; a waste steam pipe of that metal being elongated several inches in a few weeks.

A compound bar, made by riveting or soldering together two thin plates of copper and platinum, affords a good illustration of unequal expansion by heat. The copper plate, being much more expansible than platinum, the bar is bent upon the application of heat to it; and in such a manner, that the copper is on the outside of the curve. The reverse is produced when the bar is cooled. It may easily be conceived, that by a proper attention to the expansions of the metals of which it is composed, a bar of this kind might be so constructed, that although it was heated and expanded, its extreme points should always remain at the same distance from each other, the lengthening being compensated for by the bending. The balance-wheels of chronometers are preserved invariable in their diameters, at all temperatures, by a contrivance of this kind. It has also been applied to the construction of a thermometer of solid materials — that of Breguet.

FIG. 1.



When hot water is suddenly poured upon a thick plate of glass, the upper surface is heated and expanded before the heat penetrates to the lower surface of the plate. There is here unequal expansion, as in the slip of copper and platinum. The glass tends to bend, with the hot and expanded surface on the outside of the curve, but is broken from its want of flexibility. The occurrence of such fractures is best avoided by applying heat to glass vessels in a gradual manner, so as to occasion no great inequality of expansion; or by using very thin vessels, through the substance of which heat is rapidly transmitted.

This effect of heat on glass may by a little address be turned to advantage. Watch-glasses are cut out of a thin globe of glass, by conducting a crack in a proper direction, by means of an iron rod, or piece of tobacco pipe, heated to redness. Glass vessels damaged in the laboratory may often be divided in the same manner and still made available for useful purposes.

Both cast iron and glass are peculiarly liable to accidents from unequal expansion, when in the state of flat plates. Plate glass, indeed, can never be heated without risk of its breaking. The flat iron plates placed across chimneys as dampers, are also very apt to split when they become hot, and much inconvenience has often been experienced in manufactories from this cause. A slight curvature in their form has been found to protect them most effectually.

*Expansion of liquids.**—In liquids the expansive force of heat is little resisted by cohesive attraction, and is much more considerable than in solids. This fact is strikingly exhibited by filling the bulb and part of the stem of a common thermometer tube with a liquid, and applying heat to it. The liquid is seen immediately to mount in the tube.

The first law, in the case of liquids, is that some expand much more considerably by heat than others. Thus, on being heated to the same extent, namely, from the freezing to the boiling point of water—

Spirit of wine expands	$\frac{1}{9}$,	that is,	9	measures become	10
Fixed oils	$\frac{1}{12}$,	"	12	"	13
Water	$\frac{1}{22{\cdot}76}$,	"	22·76	"	23·76
Mercury	$\frac{1}{55{\cdot}5}$,	"	55·5	"	56·5

Spirit of wine is, therefore, six times more expansible by heat than mercury is. The difference in the heat of the seasons affects sensibly the bulk of spirits. In the height of summer, spirits will measure 5 per cent. more than in the depth of winter.

The new liquids produced by the condensation of gases appear to be characterized by an extraordinary dilatability. M. Thilorier has observed, that fluid carbonic acid is more expansible by heat than air itself; heated from 32° to 86°, twenty volumes of this liquid increase to twenty-nine, which is a dilatation four times greater than is produced in air, by the same change of temperature. (Annales de Chimie et de Physique, t. 60, p. 427.) Mr. Kemp extended this observation to liquid sulphurous acid and cyanogen, which, although not possessing the excessive dilatability of liquid carbonic acid, are still greatly more expansible than ordinary liquids. Sir D. Brewster had several years before discovered certain fluids in the minute cavities of topaz and quartz, which seemed to bear no analogy to any other then known liquid in their extraordinary dilatability. They do not appear to have been entirely liquefied gases, but probably were so in part. (Edinburgh Phil. Journ. vol. ix. p. 94, 1824; vol. xvi. p. 11, 1845.)

A singular correspondence has been observed, by M. Gay-Lussac, (Ann. de Chimie, t. 2, p. 130,) between two particular liquids — alcohol and bisulphuret of carbon, in the amount of their expansion by heat: although each of these liquids has a peculiar temperature at which it boils—

Alcohol at	173°
Sulphuret of carbon at	116°

still the ratios of expansions from the addition, and of contraction from the loss of heat, are found to be uniformly the same in these two liquids, compared at the same distance from their respective boiling points. A similar relation has lately been observed by M. Isidore Pierre, between the bromide of ethyl and bromide of methyl, and between the iodide of ethyl and iodide of methyl, which does not appear to exist between a pair of isomeric bodies, which were also compared,—namely, the formiate of oxide of ethyl and the acetate of oxide of methyl. The observations made with this view on four different groups of liquids, including those mentioned, are thus exhibited, the degrees of temperature being of Fahrenheit's scale:[1] —

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[1] M. Pierre has also examined the dilatations of water, oxide of ethyl (ether), and chloride of ethyl. The results he has already published are the most exact and valuable we possess on the subject of the dilatation of liquids; and he is proceeding with his experiments. Ann. de Chimie, &c., 3 série, t. 15, p. 325. 1845.

* [*See Supplement*, p. 628.]

CONTRACTION OF LIQUIDS FROM THE BOILING POINT (PIERRE).

NAMES OF THE LIQUIDS.	BOILING POINT.	TEMPERATURES equidistant from the boiling point for each group.	INTERVAL between the two preceding temperatures.	VOLUME at boiling point.	VOLUMES at the equidistant temperatures.
I. GROUP.					
Sulphuret of carbon	118·22°	—22·72°	140·94°	1	0·913099
Alcohol	172·94°	32°	140·94°	1	0·914452
Wood-spirit	151·34°	—10·4°	140·94°	1	0·905819
II. GROUP.					
Bromide of ethyl	105·26°	32°	73·26°	1	0·944375
Bromide of methyl	55·4°	—17·86°	73·26°	1	0·944575
III. GROUP.					
Iodide of ethyl	158°	32°	126°	1	0·918704
Iodide of methyl	110·84°	—15·16°	126°	1	0·916643
IV. GROUP.					
Formiate of oxide of ethyl	127·22°	—20·12°	107·1°	1	0·910223
Acetate of oxide of methyl	139·10°	—15·8° 32°	107·1°	1	0·918750

I have only to add the following results obtained by M. Muncke, of St. Petersburgh:[1]—

EXPANSION OF LIQUIDS, VOLUME AT 32° FAHR. BEING 1.

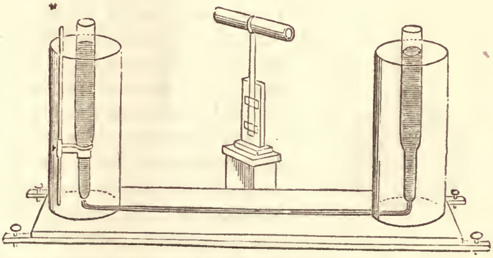
Solution of ammonia (sp. gr. 0·9465) ...	1·0198310	at 113° (45° Centig.)
Hydrochloric acid (sp. gr. 1·1978).........	1·0253598	" "
Nitric acid (sp. gr. 1·4405)	1·0479512	" "
" "	1·1148853	at 212° (100° Centig.)
Sulphuric acid (sp. gr. 1·836)	1·0578495	at 212°
" "	1·1388577	at 446° (230° Centig.)
Rectified petroleum (sp. gr. 0·7813)	1·1060059	at 203° (95° Centig.)
Almond oil	1·0787005	at 212° (100° Centig.)

The second law is, that liquids are progressively more expansible at higher than at lower temperatures. This is less the case with mercury, perhaps, than with any other liquid. The expansions of that liquid are, indeed, so uniform, as to render it extremely proper for the construction of the thermometer, as will afterwards appear. The rate of expansion of mercury was determined with extraordinary care by Dulong and Petit.

From 0° to 100°	Centigrade,	mercury	expands	1	measure on	55½
" 100° " 200°	"	"	"	1	"	54¼
" 200° " 300°	"	"	"	1	"	53

According to the same experimenters, the expansion of mercury, confined in glass tubes, is only 1 on 64·8. The dilatation of the glass causes the capacity of the instrument to be enlarged, so that the whole expansion of the mercury is not indicated. The only mode in which the error introduced by the expansion of the enclosing vessel can be

FIG. 2.



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[1] See the Handwörterbuch der Chemie of Liebig, Poggendorff, and Wöhler, vol. i. p. 632; article Ausdehnung (Dilatation).

avoided, in ascertaining the expansion of liquids, is that practised by Dulong and Petit: namely, heating the liquid in one limb of a syphon (see fig. 2), and observing how high it rises above the level of the same liquid in the other limb, kept at a constant temperature. The columns of course balance each other, and the shorter column of dense fluid supports a longer column of dilated fluid. All other modes of obtaining the absolute expansions of liquids are fallacious.

No progress has yet been made in discovering the law by which expansions of liquids are regulated; for the complicated mathematical formulæ of Biot, Dr. Young, and others, are mere general expressions for these expansions, which proceed upon no ascertained physical principle. Some theory must be formed of the constitution of liquids, before we can hope to account for their expansions.

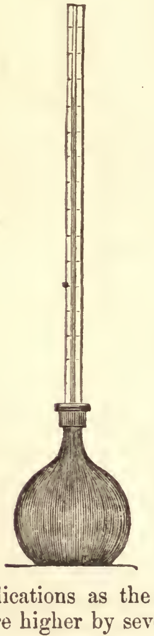
Count Rumford ascertained the contraction of water for every 22½ degrees, in cooling from 212° to 32°. The results are as follows:—

2000 measures of water contract—

In cooling 22½ degrees, or from	212°	to	189½°	18	measures.
“ “	189½	“	167	16·2	“
“ “	167	“	144½	13·8	“
“ “	144½	“	122	11·5	“
“ “	122	“	99½	9·3	“
“ “	99½	“	77	7·1	“
“ “	77	“	54½	3·9	“
“ “	54½	“	32	0·2	“

The expansion of water by heat is subject to a remarkable peculiarity, which occasions it to be extremely irregular, and demands special notice. This liquid, in a certain range of temperature, becomes an exception to the very general law that bodies expand by heat. When heat is applied to ice-cold water, or water at the temperature of 32°, this liquid, instead of expanding, contracts by every addition of heat, till its temperature rises to 40°, at or very near which temperature water is as dense as it can be. And, conversely, when water of the temperature of 40° is exposed to cold, it actually expands with the progress of the refrigeration. Water may, with caution, be cooled 20 or 25 degrees below its freezing point, in the fluid form, and still continue to expand. It is curious that this liquid, in a glass bulb, expands as nearly as possible to the same amount on each side of 40°, when either heated or cooled the same number of degrees. Hence, when cooled to 36° it rises to the same point in the stem as when heated to 44°; at 32° it stands at the same point as at 48°; at 20°, at the same point as at 60°, temperatures (fig. 3). The expansion of water by cold, under 40°, is certainly not very great, being little more than 1 part in 10,000 at 32°; hence it was early suspected that it might be an illusion, from the contraction of the glass bulb (in which the experiment was always made) forcing up the water in the stem. But all grounds of objection on this score have been removed by the mode in which the experiment has subsequently been conducted, particularly in the researches of the late Dr. Hope, of Edinburgh, on this subject. (Phil. Trans. vol. v. p. 379.)

Fig. 3.



Dr. Hope carried a deep glass jar, filled with water of the temperature of 50°, into a very cold room; and having immersed two small thermometers in the water, one near the surface, and the other at the bottom of the jar, watched their indications as the cooling proceeded. The thermometer above indicated a temperature higher by several degrees than the thermometer below, till the temperature fell to 40°, that is, the chilled water fell as usual to the bottom of the jar, or became denser as it lost heat, as illustrated in fig. 4. At 40° the two thermometers were for some time steady (fig. 5), but as the cooling proceeded beyond that point, the instrument in the higher situation indicating the lower temperature, (fig. 6); or the water now as it became colder, became lighter, and rose to the top. A better demonstration of the fact in question could not be devised.

Fig. 4.

In cooling above 40°.

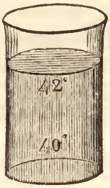


Fig. 5.

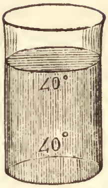


Fig. 6.

In cooling below 40°.

Great pains have been taken by several philosophers to determine the exact temperature of this turning point at which water possesses its maximum density. By the elaborate experiments of both Hällstrom and of Muncke and Stampfer, as calculated by Hällstrom, this point is 39°·38, or 4°·1 Centigrade. Rudberg has more recently obtained 4°·02 C·, and Despretz 4°·00 C., or 39°·2 Fahr., the number now generally taken. Sir C. Blagden and Mr. Gilpin had made it 39°. Dr. Hope had estimated it at 39½°.[1]

When salt is dissolved in water, the temperature of maximum density becomes lower and lower, in proportion to the quantity of salt in solution, and sinking below the freezing point of the liquid, the anomaly disappears. This is the reason why the property in question cannot be observed in sea water.

There is a solid body which presents the only other known parallel case of progressive contraction by heat; this is Rose's fusible metal, which is an alloy of—

2 parts by weight of Bismuth
1 part " " " Lead
1 " " " " Tin

A bar of this metal expands progressively, like other bodies, till it attains the temperature of 111°; it then rapidly contracts by the continued addition of heat, and at 156° attains its maximum density, occupying less space than it does at the freezing point of water. It afterwards progressively expands, melting at 201°. It may be remarked, however, of this body, that it is a chemical compound, of a kind in which a change of constitution is very likely to occur from a change in temperature; and that it cannot, therefore, be fairly compared with water.

The dilatation which water undergoes below 39° has been supposed to be connected with its sudden increase in volume in freezing, for ice is lighter than water, bulk for bulk, in the proportion of 92 to 100. The water, it is said, may begin to pass partially into the solid form at 39°, although the change is not complete till the temperature sinks to 32°. But such an assumption is altogether gratuitous, and improbable in the extreme.

The extraordinary irregularity in the dilatation of water by heat is not only curious in itself, but also of the utmost consequence in the economy of nature. When the cold sets in, the surface of our rivers and lakes is cooled by the contact of the cold air and other causes. The superficial water so cooled, sinks and gives place to warmer water from below, which, chilled in its turn, sinks in like manner. The progress of cooling in the lake goes on with considerable rapidity, so long as the cold water descends and exposes that not hitherto cooled. But this *circulation,* which accelerates the cooling of a mass of water in so extraordinary a degree, ceases entirely when the whole water has been cooled down to the temperature of 40°, which is still eight degrees above the freezing point. Thereafter the chilled surface water expands as it loses its heat, and remains at the top, from its lightness, while the cold is very imperfectly propagated downwards. The surface in the end freezes, and the ice may thicken, but at the depth of a few feet the temperature is not under

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[1] For tables of the volume of water at different temperatures, see Appendix 1.

40°, which is high when compared with that frequently experienced, even in this climate, during winter.

If water continued to become heavier, until it arrived at the freezing temperature, the whole of it would be cooled to that point before ice began to be formed; and the consequence would be, that the whole body of water would rapidly be converted into ice, to the destruction of every being that inhabits it. Our warmest summers would make but little impression upon such masses of ice; and the cheerful climate, which we at present enjoy, would be less comfortable than the frozen regions of the pole. Upon such delicate and beautiful adjustments do the order and harmony of the universe depend.

Expansion of gases. — The expansion by heat in the different forms of matter is exceedingly various.

By being heated from 32° to 212°,

1000	cubic inches of	iron	become	1004
1000	"	water	"	1045
1000	"	air	"	1366

Gases are, therefore, more expansible by heat than matter in the other two conditions of liquid and solid. The reason is, that the particles of air or gas, far from being under the influence of cohesive attraction, like solids or liquids, are actuated by a powerful repulsion for each other. The addition of heat mightily enhances this repulsive tendency, and causes great dilatation.

The rate of the expansion of air and gases from increase of temperature, was long involved in considerable uncertainty. This arose from the neglect of the early experimenters to *dry* the air or gas upon which they operated. The presence of a little water by rising in the state of steam into the gas, on the application of heat, occasioned great and irregular expansions. But in 1801, the law of the dilatation of gases was discovered by M. Gay-Lussac, of Paris, and by our countryman, Dr. Dalton, independently of each other. It was discovered by these philosophers that *all gases* experience the same increase in volume by the application of the same degree of heat, and that the rate of expansion continues uniform at all temperatures.

Dr. Dalton confined a small portion of dry air over mercury in a graduated tube. He marked the quantity by the scale, and the temperature by the thermometer. He then placed the whole in circumstances where it was uniformly heated up to a certain temperature, and observed the expansion. Gay-Lussac's apparatus was more complicated, but calculated to give very precise results. He found that 1000 volumes of air, on being heated from 32° to 212°, become 1375, which agreed very closely with Dalton's result. The expansion was lately corrected by Rudberg, who found that 1000 volumes of air expand to 1365.

The still more recent and exact researches of Magnus and of Regnault give as the expansion of air from 32° to 212°, $\frac{366.5}{1000}$, or $\frac{11}{30}$ of its volume at 32°. The dilatation for every degree of Fahrenheit is 0·002036 (Regnault); or $\frac{1}{491.2}$ part.

It follows, consequently, that air at the freezing point expands $\frac{1}{491}$ part of its bulk for every added degree of heat on Fahrenheit's scale: that is —

491	cubic inches of air	at	32° become
492	"	"	33°
493	"	"	34°, &c.

increasing one cubic inch for every degree. A contraction of one cubic inch occurs for every degree below 32°.

491	cubic inches of air	at	32° become
490	"	"	31°
489	"	"	30°
488	"	"	29°, &c.

We can easily deduce, from this law, the expansion which a certain volume of gas at a given temperature will undergo, by heating it up to any particular temperature;

or the contraction that will result from cooling.[1] Air of the temperature of freezing water, has its volume doubled when heated 491 degrees, and when heated 982 degrees, or twice as intensely, its volume is tripled, which is the effect of a low red heat.

A slight deviation from exact uniformity in the expansion of different gases was established by the rigorous experiments of both Magnus (Ann. de Chim. &c. 3 sér. t. 4, p. 330; et t. 6, p. 353) and Regnault (ibid. t. 4, p. 5; et t. 6, p. 370). The more easily liquefied gases, which exhibit a sensible departure from the law of Mariotte, are more expansible by heat than air, as will appear by the following table:—

Names of the Gases.	Expansion upon 1 volume from 32° to 212°.	
	Regnault.	Magnus.
Atmospheric air	0·36650	0·366508
Hydrogen	0·36678	0·365659
Carbonic acid	0·36896	0·369087
Sulphurous acid	0·36696	9·385618
Nitrogen	0·36682	
Nitrous oxide	0·36763	
Carbonic oxide	0·36667	
Cyanogen	0·36821	
Hydrochloric acid	0·36812	

The expansion is also found to be sensibly greater when the gas is in a compressed than when in a rare state; and the results above strictly apply only to the gases under the atmospheric pressure.

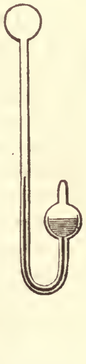
THE THERMOMETER,

An instrument for indicating variations in the intensity of heat, or degrees of temperature, by their effect in expanding some body, was invented more than two centuries ago, and has received successive improvements.

The expansions of solids are too minute to be easily measured, and cannot, therefore, be conveniently applied to mark degrees of heat. Air and gases, on the other hand, are so much dilated by a slight increase of heat, that they are not calculated for ordinary purposes. The first thermometer constructed, however, that of Sanctorio, was an air one. A glass tube, open at one end, with a bulb blown upon the other (fig. 7), was slightly heated, so as to expel a portion of the air from it, and then the open end of the tube was dipped under the surface of a coloured fluid, which was allowed to rise into the tube, as the air cooled and contracted. When heat, the heat of the hand for instance, is applied to the bulb, the air in it is expanded, and depresses the column of coloured fluid in the tube. A useful modification of the air thermometer, for researches of great delicacy, was contrived by Sir John Leslie, under the name of the Differential Thermometer. In this instrument two close bulbs are connected by a syphon containing a coloured liquid (fig. 8). If both bulbs be equally heated, the air in each is equally expanded, and the liquid between them remains stationary. But if the upper bulb only be heated, then the air in that bulb is expanded, and the column of liquid depressed. It is, therefore, the difference of temperature between the two bulbs which is indicated.

Fig. 7.

Fig. 8.



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[1] As 491 cubic inches of air at 32° become 459 cubic inches at 0°, air may be stated to expand $\frac{1}{459}$th part of its volume at the zero of Fahrenheit for each degree. That is, 459 volumes of air at 0° become at 50°, 459 + 50 volumes, or 509 volumes; at 60°, 459 + 60 volumes, or 519 volumes. Hence the expansion of 100 volumes of air from 50° to 60° is obtained by the proportion—

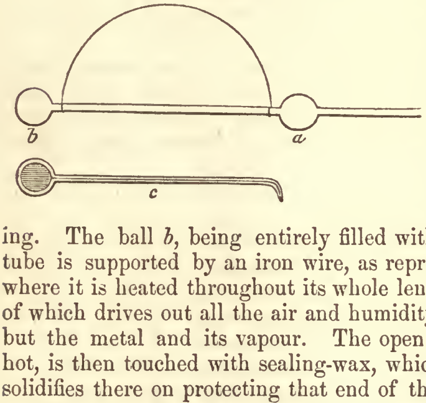
Meas. at 50°.		Meas. at 60°.		Meas. at 50°.		Meas. at 60°.
509	:	519	::	100	:	101·96

But liquids fortunately are intermediate in their expansions between solids and gases, and when contained in a glass vessel of a proper form, the changes of bulk which they undergo can be indicated to any degree of precision.

A hollow glass stem or tube is selected, the calibre or bore of which may be of any convenient size, but must be uniform, or not wider at one place than another. Tubes of very narrow bore, and which are called *capillary*, the bore being like a hair in magnitude, are now alone employed. Such tubes are made by rapidly drawing out a hollow mass of glass while soft and ductile under the influence of heat. The central cavity still continues, becoming the bore of the tube, and would not cease to exist although the tube were drawn out into the finest thread. From the mode in which capillary tubes are made, their equality of bore, and suitableness for thermometers, cannot always be depended upon. The bore is frequently conical, or wider at one end than at the other. It is tested by drawing up into the tube a little mercury, as much as fills a few lines of the cavity. The little column is then moved progressively along the tube, and its length accurately measured, at every stage, by a pair of compasses. The column will measure the same in every part of the tube, provided the bore does not alter. Not more than one-sixth part of the tubes made are found to possess this requisite.

Satisfied with the regularity of the bore, the thermometer-maker softens one extremity of the tube, and blows a ball upon it. This is not done by the mouth, which would moisten the interior, by introducing watery vapour, but by means of an elastic bag of caoutchouc, which is fitted to the open end of the tube. He then marks off the length which the thermometer ought to have, and above that point expands the tube into a second bulb a little larger than the first. It has the form of fig. 9. After cooling, the open extremity of the tube is plunged into distilled and well-boiled mercury, and one of the bulbs heated so as to expel air from it. During the cooling, the mercury is drawn up and rises into the ball *a*. It is made to pass from thence into the ball *b*, by turning the instrument, so that *b* is undermost, and then expelling the air from that bulb by applying heat to it, after which the mercury descends, from the effect of cooling. The ball *b*, being entirely filled with mercury, and a portion left in *a*, the tube is supported by an iron wire, as represented in the figure, over a charcoal fire, where it is heated throughout its whole length, so as to boil the mercury, the vapour of which drives out all the air and humidity, and the balls contain at the end nothing but the metal and its vapour. The open end of the tube, which must not be too hot, is then touched with sealing-wax, which is drawn into the tube on melting, and solidifies there on protecting that end of the tube from the heat. That being done, the thermometer is immediately withdrawn from the fire, and being held with the end sealed with wax uppermost, during the cooling the ball *b*, and the portion of the tube below the ball *a*, are filled with mercury. After cooling, the instrument is inclined a little, and by warming the lower ball, a portion of mercury is expelled from it, so that the mercury may afterwards stand at a proper height in the tube when the instrument is cold. The tube is then melted with care by the blow-pipe flame below the ball *a*, and closed, or hermetically sealed, as in *c*. The thermometer is in this way properly filled with mercury, and contains no air.

FIG. 9.



We have now an instrument in which we can nicely measure and compare any change in the bulk of the included fluid metal. Having previously made sure of the equality of the bore, it is evident that if the mercury swells up and rises two, three, four, or five inches in the tube, it has expanded twice, thrice, four, or five times more than if it had risen only one inch in the tube. By placing a graduated scale against the tube, we can therefore learn the quantity of expansion by simple inspection.

In order to have a fixed point on the scale, from which to begin counting the expansion of mercury by heat, we plunge the bulb of the thermometer into melting ice, and put a mark on the stem at the point to which the mercury falls. However frequently we do so with the same instrument, we shall find that the mercury always falls to the same point. This is, therefore, a fixed starting point. We obtain another fixed point by plunging the thermometer into boiling water. With certain precautions, this point will be found equally fixed on every repetition of the experiment. The most important of these precautions is, that the barometer be observed to stand at 30 inches,[1] when the boiling point is taken. It will afterwards be explained that the boiling point of water varies with the atmospheric pressure to which it is subject at the time.

Thermometers which are properly closed, and contain no air, can be inverted without injury, and the mercury falls into the tube, producing a sound as water does in the water-hammer. When the instrument contains air, the thread of mercury is apt to divide on inversion, or from other circumstances. When this accident occurs, it is best remedied by attaching a string to the upper end of the instrument, and whirling it round the head. The detached little column of mercury generally acquires in this way a centrifugal force, which enables it to pass the air, and rejoin the mercury in the bulb.

When the glass of the bulb is thin, it is proper to seal the tube as described, and to retain it for a few weeks before marking upon it the fixed points. Thermometers, however carefully graduated at first, are found in a short time to stand above the mark in melting ice, unless this precaution be attended to. Old instruments often err by as much as half a degree, or even a degree and a half, in this way.[2] The effect is supposed to arise from the pressure of the atmosphere upon the bulb, which, when not truly spherical, seems to yield slightly, and in a gradual manner. The chance of this defect may be avoided by giving the bulb a certain thickness. Mr. Crichton's thermometers, of which the freezing point has not altered in forty years, were all made unusually thick in the glass. But this thickness has the disadvantage of diminishing the sensibility of the instrument to the impression of heat.

We have in this way the expansion marked off on the tube, which takes place between the freezing and boiling points of water. On the thermometer which is used in this country, and called Fahrenheit's, this space is subdivided into 180 equal parts, which are called degrees. This division appears empirical, and different reasons are given why it was originally adopted. But as Fahrenheit, who was an instrument-maker in Amsterdam, kept his process for graduating thermometers a secret, we can only form conjectures as to what were the principles that guided him.

It is more convenient to divide the space between the freezing and boiling of water into 100 equal parts, which was done in the instrument of Celsius, a Swedish philosopher. This division was adopted at a later period in France, under the designation of the Centigrade scale, and is now generally used over the continent. The freezing point of water is called 0, or zero, and the boiling point 100. But in our scale, the point is arbitrarily called 32°, or the 32d degree; and consequently the boiling point is 32 added to 180, or the 212th degree.[3]

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[1] More exactly 29·92 inches, that is, 760 millimètres; the latter number being universally assumed on the continent as the standard height of the barometer.

[2] Many thermometers cannot be heated 60 or 80 degrees, without a sensible displacement of the zero point, as remarked by Regnault (Ann. de Chimie, &c., 3 sér., t. 6, p. 378), and by Is. Pierre (Ib. 3 sér., t. 5, p. 427; et t. 15, p. 332), who indicate the extraordinary precautions requisite in the construction of thermometers for accurate research.

[3] A simple rule may be given for converting Centigrade degrees into degrees Fahrenheit. 100 degrees Centigrade being equal to 180 degrees Fahrenheit, 10 degrees C. = 18 degrees

The scale can easily be prolonged to any extent, above or below these points, by marking off equal lengths of the tube for 180 degrees, either above or below the space first marked. The degrees of contraction below zero, or 0°, are marked by the minus sign (—), and called negative degrees, in order to distinguish them from degrees of the same name above zero, or positive degrees. Thus, 47° means the 47th degree above zero, —47°, the 47th degree under zero.

The only other scale in use is that of Reaumur, in the north of Germany. The expansion between the freezing and boiling of water is divided into 80 parts in this thermometer. The relation between the three scales is illustrated in the following diagram.

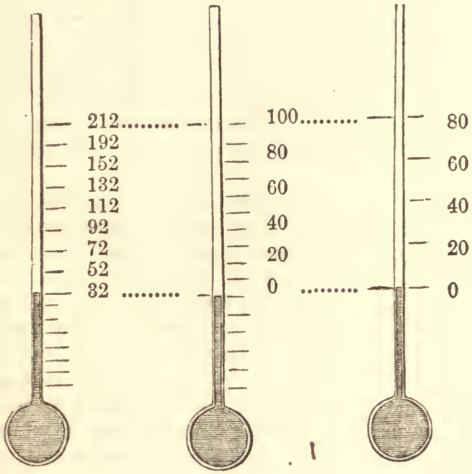

Fig. 10. Fahrenheit's scale.

Fig. 11. Centigrade scale.

Fig. 12. Reaumur's scale.

The zero of our scale is 32 degrees below the freezing point of water, and the expansions of mercury are available in the thermometer from —39° to 600°; but about the latter degree, mercury rises in the tube in the state of vapour, so as to derange the indications, and at about 660° it boils, and can no longer be retained in the glass vessel; while at the former low point it freezes or becomes solid. For degrees of cold below the freezing point of mercury, we must be guided by the contractions of alcohol or spirits of wine, a liquid which has not been frozen by any degree of cold we are capable of producing. There is no reason, however, for believing that we have ever descended more than 160 or 170 degrees below zero of Fahrenheit.

The zero of these scales has, therefore, no relation to the *real zero* of heat, or point at which bodies have lost all heat. Of this point we know nothing, and there is no reason to suppose that we have ever approached it. The scale of temperature may be compared to a chain, extended both upwards and downwards beyond our sight. We fix upon a particular link, and count upwards and downwards from that link, and not from the beginning of the chain.

The means of producing heat are much more at our command, but we have no measure of it, of easy application and admitted accuracy, above the boiling point of mercury. Recourse has been had to the expansion of solids at high temperatures, and various pyrometers, or "measures of fire," have been proposed. Professor

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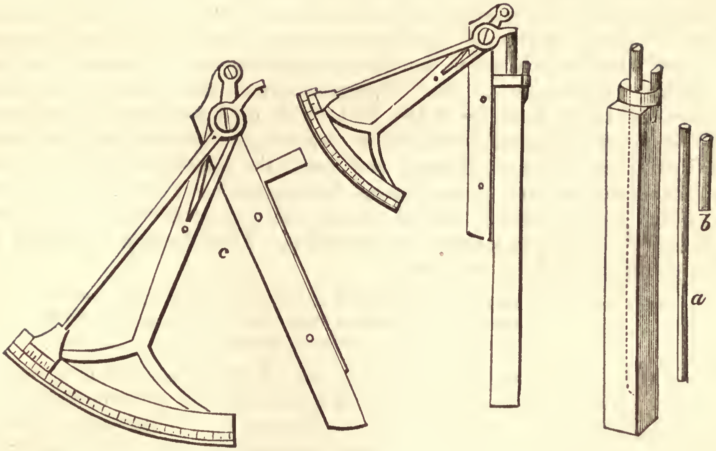
F., or 5 degrees C. = 9 degrees F.; multiply the Centigrade degrees by 9, and divide by 5, and add 32. Thus to find the degree F. corresponding with 50° C.

$$\begin{array}{r} 50 \\ 9 \\ \hline 5)450 \\ \hline 90 \\ \text{add } 32 \\ \hline \end{array}$$

Or the 50° C. corresponds with the 122° F.

For facility of reference a table of the corresponding degrees is given in Appendix II.

Fig. 13.



Daniell's pyrometer is a valuable instrument of this kind, of which the indications result from the difference in the expansion by heat of an iron or platinum bar, and a tube of well-baked black-lead ware, in which the bar is contained. The metallic bar *a* is shorter than the tube, and a short plug of earthenware *b* is placed in the mouth of the tube above the iron bar, and so secured by a strap of platinum foil and a little wedge, that it slides with difficulty in the tube. By the expansion of the metallic bar, the plug of earthenware is pushed outwards, and remains in its new position after the contraction of the metallic bar on cooling. The expansion of the iron bar thus obtained, is measured by adapting to the instrument an index, *c*, which traverses a circular scale, before and after the earthenware plug has been moved outwards by the expansion of the metallic bar. The degrees marked on the scale are in each instrument compared experimentally with those of the mercurial scale, and the ratio marked on the instrument, so that its degrees are convertible into those of Fahrenheit, (Philosophical Transactions, 1830–31). An air thermometer, of which the bulb and tube were of metal, has also been employed to explore high temperatures. In the old pyrometer of Wedgwood, the degree of heat was estimated by the permanent contraction which it produced upon a pellet of pipe-clay; but the indications of this instrument are fallacious, and it has long gone out of use.

The applicability of the mercurial thermometer to measure degrees of heat, depends upon two important circumstances, which involve the whole theory of the instrument:—

1st. The hollow glass ball, with its fine tube of uniform bore, is a nice fluid measure. The ball and part of the stem being filled with a fluid, the slightest change in the bulk of the fluid, which may arise from the application of heat or of cold to it, is conspicuously exhibited by the rise or fall of the fluid column in the stem. No more delicate measure of the bulk of an included fluid could be devised.

2d. It fortunately happens that the expansions of mercury, which can thus be measured so accurately, are proportional to the quantities of heat which produce them. But the mode in which this is proved requires a little attention. Suppose we had two reservoirs, one containing cold, and the other hot water. Plunge a thermometric bulb containing mercury first into the cold water, and mark at what point in the stem the mercury stands. Then plunge it into the hot water, and mark also the point to which the mercury now rises in the stem. We can obviously make a heat which will be half way exactly between the hot and cold water, by taking the same quantity of the hot and cold water, and mixing them together. Now, does this half heat produce a half expansion in mercury? On trial we find that it does. In the mixture of equal parts of the hot and cold water, the mercury stands exactly half way between the marks, supposing the experiment to be conducted with the proper precautions. This proves that the dilatations of mercury are proportional to the intensity of the heat which produces them. In the mercurial thermometer, therefore, quantities or degrees of expansion may be taken to indicate quantities or degrees of heat; and that is the principle of the instrument.

The same correspondence exists between the expansions of *air* and the quantities of heat which produce them. Indeed, in air, the correspondence is rigidly exact, while in mercury it is only a close approximation. Thus Dulong and Petit found that the boiling point of mercury was,

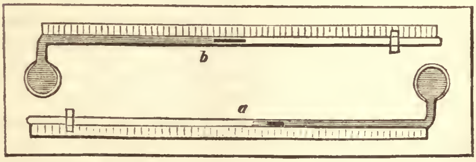
As measured by mercury in a syphon	680°
" " the air thermometer (true temp.)	662°
" " mercury in glass (Mr. Crichton)	660°

A short table exhibiting the increasing rate of the expansions of mercury has already been given, but glass expands in a ratio increasing quite as rapidly as this metal; so that the greater expansion of the mercury in the thermometer at high temperatures is fortunately corrected by the increasing capacity of the glass bulb.[1]

Fixed oils and spirit of wine do not deviate far from uniformity in their expansions, at least at low temperatures, and therefore are sometimes used as thermometric liquids. Spirit of wine thermometers, however, are often found to vary 6 or 8 degrees from each other at temperatures so low as —30° or —40°.

Thermometers have been devised which indicate the highest and lowest temperature which has occurred between two observations, or are self-registering. A thermometer, which was invented by Dr. Rutherford, is of this kind. This instrument consists, properly speaking, of two thermometers, one, *a*, of spirit of wine, and the other, *b*, of mercury, which are placed in the position represented in the figure, their stems being horizontal. The thermometer *b* is intended to indicate the maximum temperature. It contains, in advance of the mercury, a short piece of iron wire, which the mercury carries forward with it in dilating, and which remains in its advanced position, marking the highest temperature that has occurred, when the mercury withdraws. The minimum temperature is indicated by the spirit of wine thermometer *a*, which contains, immersed in the spirit, a small cylinder of ivory, or enamel, which, by a slight inclination of the instrument, falls to the surface of the liquid without being able to pass out of it. When the thermometer sinks, the ivory is carried back in the spirit; but when the temperature rises, the alcohol only advances, leaving the ivory where it was. Its extremity most distant from the bulb then indicates the lowest temperature to which the thermometer had been exposed. Before another observation is made, the ivory must be brought again to the surface of the alcohol by a slight percussion of the instrument.

Fig. 14.



Another self-registering instrument, known in London as Six's, has the great advantage over the preceding instrument of being much less liable to go out of order. It consists of one thermometer only (fig. 15), filled with colourless spirit of wine, having a large cylindrical bulb. The stem is twice bent, and contains a column of mercury, *b*, in the lower bend, which is in contact with the alcohol, and

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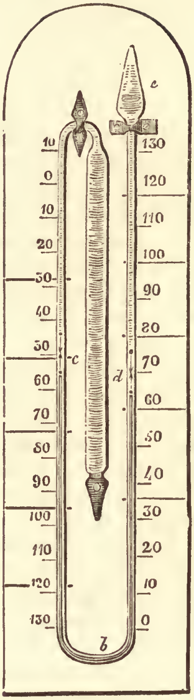
[1] In a note on the Comparison of the Air and Mercurial Thermometers; by M. Regnault. Annales de Chimie, &c. 3 sér. t. 6, p. 470.

advances or recedes with it. On either side of this mercury there is placed a little iron cylinder, or index, *c* and *d*, which has a fine hair projecting from it, so as to press against the sides of the tube, and cause the cylinder to move with a little difficulty. These iron cylinders, which have flattened ends covered with a vitreous matter, are brought into contact with the mercury by means of a magnet, and are pushed along by the column of mercury, when the latter is moved by the alcohol. The minimum temperature is indicated by *c*, and the maximum by *d*. The tube is expanded at *e*, and sealed after filling that space partly with alcohol, for no other purpose than to facilitate the movement of the index; *d*.

Fig. 15.



Our notions of the range of temperature acquire all their precision from the use of the thermometer. Cold, for instance, is allowed a substantial existence, as well as heat, in popular language. What is cold? it is the absence of heat, as darkness is the absence of light. The absence of heat, however, is never complete, but only partial. Water, after it is frozen into ice, cold as it is in relation to our bodies, has not lost all its heat, for it is easy to cool a thermometer far below the temperature of ice, and have it in such a condition as that it shall acquire heat, and be expanded by contact with ice; thus proving that the ice contains heat. Spirits of wine have not been frozen at the lowest temperature that has hitherto been attained; but even then this liquid possesses heat, and there is no doubt that if a sufficiently large portion of its heat were withdrawn, it would freeze like other bodies. The following are interesting circumstances in the range of temperature —

—220°	Fahr.	Greatest artificial cold measured. (Natterer.)
—166°	"	" " " " (Faraday.)
—150°	"	Liquid nitrous oxide freezes. ‘
—122°	"	Liquid sulphuretted hydrogen freezes. "
—105°	"	Liquid sulphurous acid freezes. "
— 71°	"	Liquid carbonic acid freezes. "
— 91°	"	Greatest artificial cold measured by Walker.
— 56°	"	Greatest natural cold observed by a "verified" thermometer. (Sabine.)
— 70°	"	Greatest natural cold observed at Fort Reliance by Back. Doubtful.
— 58°	"	Estimated temperature of planetary space. (Fourier.)
— 47°	"	Sulphuric ether freezes.
— 39°	"	Mercury freezes.
— 30°	"	Liquid cyanogen freezes. (Faraday.)
— 7°	"	A mixture of equal parts of alcohol and water freezes.
+ 7°	"	A mixture of one part of alcohol and three parts of water freezes.
20°	"	Strong wine freezes.
32°	"	Ice melts.
50°·7	"	Mean temperature of London.
81°·5	"	Mean temperature at the Equator.
98°	"	Heat of the human blood.
117°·3	"	Highest natural temperature observed — of a hot wind in Upper Egypt. (Burckhardt.)
151°·34	"	Wood-spirit boils. (Is. Pierre.)
172°·94	"	Alcohol boils. "
212°	"	Water boils.
442°	"	Tin melts.
594°	"	Lead melts.
662°	"	Mercury boils.
980°	"	Red heat. (Daniell.)

1141°	Fahr.	Heat of a common fire.	(Daniell.)
1869°	"	Brass melts.	"
2283°	"	Silver melts.	"
3479°	"	Cast iron melts.	"

SPECIFIC HEAT.*

Equal bulks of different substances, such as water and mercury, require the addition of different quantities of heat to produce the same change in their temperature. This appears evident from a variety of circumstances. If two similar glass bulbs, like thermometers, one containing mercury and the other water, be immersed at the same time in a hot water-bath, it will be found that the mercury bulb is heated up to the temperature of the water-bath in half the time that the water bulb requires; and if the two bulbs, after having both attained the temperature of the water-bath, be removed from it and exposed to the air, the mercury bulb will cool twice as rapidly as the other. These effects must arise from the mercury absorbing only half the quantity of heat which the water does in being heated up to the same degree in the water-bath, and from having, consequently, only half the quantity of heat to lose in the subsequent cooling. Again, if we mix equal measures of water at 70° and 130°, the temperature of the whole will be 100°; or the hot measure of water, in losing 30°, elevates the temperature of the cold measure by an equal amount. But if we substitute for the hot water, in this experiment, an equal measure of mercury at 130°, on mixing it with the measure of water at 70°, the temperature of the whole will not be 100°, but more nearly 90°. Here the mercury is cooled from 130° to 90°, or loses 40° of heat, which have been transferred to the water, but which raise the temperature of the latter only 20°, or from 70° to 90°. To heat the measure of water at 70° to 100°, we must mix with it two, or a little more than two, equal measures of mercury at 130°, although one measure of water at 130° would answer the purpose. If, therefore, *two* measures of mercury, by losing 30° of temperature, heat only *one* measure of water 30°, it follows that hot mercury possesses only half the heat of equally hot water; or that water requires double the quantity of heat that is required by mercury, to raise it a certain number of degrees. This is expressed by saying that water has twice the *capacity for heat* that mercury possesses.

It is more convenient to express the capacities of different bodies for heat, with reference to equal weights than equal measures of the bodies. On accurate trial, it is found that a pound of water absorbs thirty times more heat than a pound of mercury, in being heated the same number of degrees: the capacity of water for heat is, therefore, thirty times greater than that of mercury. The capacities of these two bodies are in the relation of 1000 to 33; and it is convenient to express the capacities for heat of all bodies, in relation to that of water, as 1000. Such numbers are the *specific heats* of bodies.

There are two methods usually followed in determining capacity for heat. The first, which was that practised by MM. Dulong and Petit, consists in allowing different substances to cool the same number of degrees in circumstances which are exactly similar; to inclose them, for instance, in a polished silver vessel, containing the bulb of a thermometer in its centre, and to place this vessel under a bell-jar in which a vacuum is made. The time which the different substances take to cool, enables us to calculate the quantity of heat which they give out. The second, or method of mixture, consists in heating up the metal or other substance to 212°, and then throwing it into a vessel containing a considerable weight of cold water, to which a quantity of heat will be communicated, and a rise of temperature occasioned proportional to the capacity for heat of the substance. The following table contains results of M. Regnault, which closely coincide with the prior determinations of Dulong and Petit: —

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* [*See Supplement*, p. 640.]

Substances.	Specific heat of equal weights.
Water	1000
Ice[1]	513
Oil of turpentine, at 63·5° Fahr	426[2]
" " at 50° "	414
Wood charcoal	241[2]
Sulphur	203
Glass	198
Diamond	147[2]
Iron	113·79
Nickel	108·63
Cobalt	106·96
Zinc	95·55
Copper	95·15
Arsenic	81·40
Silver	57·01
Tin	56·23
Iodine	54·12
Antimony	50·77
Gold	32·44
Platinum	32·43
Mercury	33·32
Lead	31·40
Bismuth	30·84

The method of cooling gives results so exact, as to allow the detection of an increase of capacity with the temperature. The capacity of iron, when tried between 32° and 212°, as was the case with all the bodies in the table, was 110; but 115 between 32° and 392°, and 126 between 32° and 662°. It hence follows, that the capacity for heat, like dilatation, augments in proportion as the temperature is elevated. Dulong and Petit likewise established a relation between the capacity for heat of metallic bodies and the proportion by weight in which they combine with oxygen, or any other substance, which will again be adverted to.

Of all liquid or solid bodies, water has much the greatest capacity for heat. Hence the sea, which covers so large a proportion of the globe, is a great magazine of heat, and has a beneficial influence in equalizing atmospheric temperature. Mercury has a small specific heat, so that it is quickly heated or cooled, another property which recommends it as a liquid for the thermometer, imparting, as it does, great sensibility to the instrument.

The determination of the specific heat of gases is a problem involved in the greatest practical difficulties; so that notwithstanding its having occupied the attention of some of the ablest chemists, our knowledge on the subject is still of the most uncertain nature. It has been concluded by Delarive and Marcet (Annales de Ch. et de Ph. t. 35, p. 5; t. 41, p. 78; and t. 75, p. 113), and by Mr. Haycraft (Edinburgh Phil. Journ. vol. x. p. 351), that the specific heat of all gases is the same for equal volumes. But this opinion has been controverted by Dulong (Annales de Ch. et de Ph. t. 41, p. 113), by Dr. Apjohn (Transactions of the Royal Irish Academy, 1837), and by Suermann (Ann. de Ch. et de Ph. t. 63, p. 315), who have followed Delaroche and Berard in this inquiry (Annales de Chimie, t. 75; or Annals of Philosophy, vol. ii.) Their method was to transmit known quantities of the gases, heated to 212° in an uniform current, through a serpentine tube, surrounded by water, the temperature of which was observed, by a delicate thermometer at the beginning and end of the process. The results obtained by the different experimenters are contained in the following table: —

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[1] Ed. Desains, Annales de Chimie et de Physique, 3me sér. t. 14, p. 306 (1845). By another method, the number 465 was obtained. The capacity of ice is, therefore, sensibly one-half that of water. This is a valuable paper, which will be referred to with advantage.

[2] Regnault, ibid. t. ix. pp. 339 and 324.

SPECIFIC HEAT OF GASES.

Name of the gas.	Capacity for equal volumes. Air = 1.	Capacity for equal weights.		Authority.
		Air = 1.	Water = 1.	
Air	1·0000	1·0000	0·2669	Delaroche and Berard.
			0·3046	Suermann.
Oxygen	0·8080	0·7328	0·1956	Apjohn.
	0·9765	0·8848	0·2361	Delaroche and Berard.
	0·9954	0·9028	0·2750	Suermann.
	1·0000	0·9069	......	Delarive and Marcet, Haycraft, Dulong.
Hydrogen	0·9033	12·3401	3·2936	Delaroche and Berard.
	1·0000	14·4930	......	D. and M., Haycraft, Dulong.
	1·3979	20·3121	6·1892	Suermann.
	1·4590	21·2064	......	Apjohn.
Chlorine	1·0000	0·4074	......	Delarive and Marcet.
Nitrogen	1·0000	1·0318	0·2754	Delaroche and Berard.
	1·0005	1·0293	0·3138	Suermann.
	1·0480	1·0741	......	Apjohn.
Steam	1·9600	3·1360	0·8470	Delaroche and Berard.
Carbonic oxide	0·9925	1·0253	0·3123	Suermann.
	0·9960	1·0239	......	Apjohn.
	1·0000	1·0802	......	D. and M., Dulong.
	1·0340	1·0805	0·2884	Delaroche and Berard.
Carbonic acid	1·0000	0·6557	......	Haycraft.
	1·0655	0·6925	0·2124	Suermann.
	1·1750	......	......	Dulong.
	1·1950	0·7838	......	Apjohn.
	1·2220	......	......	Delarive and Marcet.
	1·2583	0·8280	0·2210	Delaroche and Berard.
Sulphurous acid	1·0000	0·4507	......	Delarive and Marcet.
Sulphuretted hydrog.	1·0000	0·8485	......	“ “
Hydrochloric acid	1·0000	0·7925	......	“ “
Nitrous oxide	1·0000	0·6557	......	“ “
	1·0229	0·7354	0·2240	Suermann.
	1·1600	......	......	Dulong.
	1·1930	0·7827	......	Apjohn.
	1·3503	0·8878	0·2369	Delaroche and Berard.
Nitric oxide	1·7000	0·9616	......	Delarive and Marcet.
Ammonia	1·0000	1·6968	......	“ “
Cyanogen	1·0000	0·5547	......	“ “
Olefiant gas	1.0660	......	......	Haycraft.
	1·5310	......	......	Dulong.
	1·5530	1·5763	0·4207	Delaroche and Berard.
	1·5300	......	......	Delarive and Marcet.

It will be observed, that the capacity for heat of steam, as well as of ice, is less than that of an equal weight of water. Hence the specific heat of a body may change with its physical state. Delaroche and Berard likewise observed that the capacity of a gas is increased by its rarefaction. When the volume of a gas is doubled, by withdrawing half the pressure upon it, its specific heat is not quite so much as doubled. This is the reason why a gas becomes cold in expanding. In the expanded state it requires more heat to sustain it at its former temperature, from the augmentation which has occurred in its capacity. Air expanded into double its volume is cooled 40 or 50 degrees; and it has its temperature raised to that extent by compression into half its volume; suddenly condensed to one-fifth of its volume by a piston in a small cylinder, so much heat is evolved as to cause the ignition of a readily inflammable substance, such as tinder.

COMMUNICATION OF HEAT BY CONDUCTION AND RADIATION.

1. *Conduction.**—When one extremity of a bar of iron is plunged into a fire, the heat passes through the bar in a gradual manner, being communicated from particle to particle, and after passing through the whole length of the bar, may arrive at the other extremity. Heat, when conveyed in this way, is said to be conducted.

In solid substances, the phenomenon of the conduction of heat is so simple and familiar, that little need be said on the subject. Different solid substances vary exceedingly from each other in their power to conduct heat. Dense or heavy substances are generally good conductors, while light and porous bodies conduct heat imperfectly. Hence the universal use of substances of the latter class for the purposes of clothing. Count Rumford observed, that the finer the fabric of woollen cloth is, the more imperfectly does it conduct (Phil. Trans. 1792). The down of the eider-duck appears to be unrivalled in this respect. Bad conductors are also the most suitable for keeping bodies cool, protecting them from the access of heat. Hence to preserve ice in summer, we wrap it in flannel. Among good conductors of heat, the metals are the best. The relative conducting power of several bodies is expressed by the numbers in the following table, from the experiments of Despretz (Ann. de. Ch. et Ph. t. xxxvi. p. 422): —

Gold	1000	Tin	303·9
Silver	973	Lead	179·6
Copper	898	Marble	23·6
Iron	374·3	Porcelain	14·2
Zinc	363	Clay	11·4

Glass is an imperfect conductor, for we can fuse the point of a glass rod in a lamp, holding it within an inch of the extremity. On the contrary, we find it difficult to heat any part of a thick metallic wire to redness in a lamp, owing to the rapidity with which the heat is carried away by the contiguous parts.

The following table of the conducting power of various materials used in the construction of houses, as observed by Mr. Hutchinson, is of considerable utility for practical purposes. The substances are arranged in the order in which they resist most the passage of heat; the warmest substances, which are most valuable in construction, being placed first.[1]

Name of Substance.	Conducting power referred to that of slate = 100.	Name of Substance.	Conducting power referred to that of slate = 100.
Plaster and Sand	18·70	Bath Stone	61·08
Keene's Cement	19·01	Fire Brick	61·70
Plaster of Paris	20·26	Painswick Stone (H. P.)	71·36
Roman Cement	20·88	Malm Brick	72·92
Beech Wood	22·44	Portland Stone	75·10
Lath and Plaster	25·55	Lunelle Marble	75·41
Fir Wood	27·61	Bolsover Stone (H. P.)	76·35
Oak Wood	33·66	Norfal Stone (H. P.)	95·36
Asphalt	45·19	Slate	100·00
Chalk (soft)	56·38	Yorkshire Flag	110·94
Napoleon Marble	58·27	Lead	521·34
Stock Brick	60·14		

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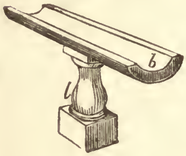
[1] New Experiments on Building Materials, by J. Hutchinson: Taylor and Walton. The three substances marked H. P. are the building stones employed in the construction of the New Houses of Parliament.

* [*See Supplement,* p. 649.]

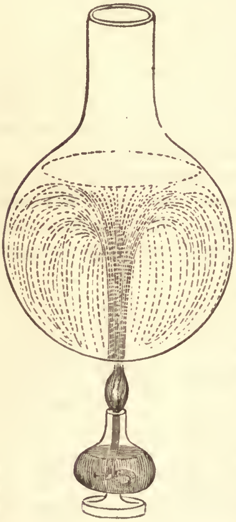
Certain vibrations were observed by Mr. Trevelyan to take place between metallic masses having different temperatures, occasioning particular sounds, which appear to be connected with the conducting power of the metal (Phil. Mag. 3d Series, vol. iii. 321). Thus, if a heated curved bar of brass *b*, be laid upon a cold support of lead *l*, of which the surface is flat, as represented in the figure, the brass bar, while communicating its heat to the lead, is thrown into a state of vibration, accompanied with a rocking motion and the production of a musical note, like that of the glass harmonicon. The rocking motion of the brass bar, accidentally commenced, appears to be continued from a repulsion which exists between heated surfaces, enhanced in this case by the low conducting power of the lead, which allows its surface to be strongly heated by the brass. Professor Forbes finds that the most intense vibrations are produced between the best conductors and the worst conductors of heat, the latter being the cold bodies (Edinburgh Phil. Trans. vol. xii.)

FIG. 16.



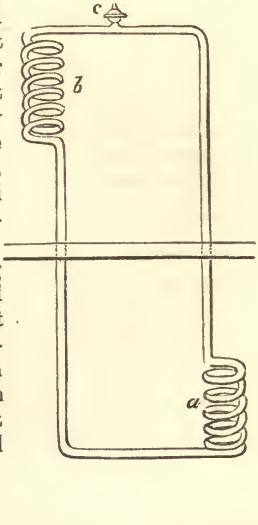
Our ordinary conceptions of the actual temperature of different bodies are much affected by their conducting power. If we apply the hand, at the same time, to a good and to a bad conductor, such as a metal and a piece of wood, which are exactly of the same temperature by the thermometer, the good conductor will feel colder or hotter than the other, from the greater rapidity with which it conducts away heat from, or communicates heat, to our body, according as the temperature of the metal and wood happens to be above or below that of the hand applied to them.

FIG. 17.



The diffusion of heat through liquids and gases is effected, in a great measure, by the motion of their particles among each other. When heat is applied to the lower part of a mass of liquid, the heated portions become lighter than the rest, and ascend rapidly, conveying or carrying the heat through the mass of the fluid. In a glass flask, for instance, containing water, with which a small quantity of any light insoluble powder has been mixed, a circulation of the fluid may be observed upon the application of the flame of a lamp to the bottom of the vessel, the heated liquid rising in the centre of the vessel, and afterwards descending near its sides, as represented in the annexed figure. But when heat is applied to the surface of a liquid, this circulation does not occur, and the heat is propagated very imperfectly downwards. It has even been doubted whether liquids conduct heat downwards at all, or, indeed, in any other way than by conveying it as above described. It can be proved, however, that heat passes downwards in fluid mercury, and hence it is probable that all liquids possess a slight conducting power similar to that of solids.

FIG. 18.



Let the endless tube represented in the accompanying figure be supposed to be entirely filled with water, and the heat of a fire be applied to the lower portion of it at *a*, which is twisted into a spiral form, the water will immediately be set in motion, and made to circulate through the tube, from the expansion and ascent of the portion in *a*, and the whole of the water in the tube will be brought in succession to the source of heat. The tube may be led into an apartment above *d*, and being twisted into another spiral at *b*, a quantity of the heat of the circulating water will be discharged in proportion to the extent of surface of tube exposed. Water of a temperature considerably above 212° is made to circulate in this manner through a very strong drawn-iron tube of about one inch in diameter, for the purpose of heating houses and public buildings. A slight waste of the water is found to occur, so that it is necessary to introduce a small quantity every few weeks by an opening and stopcock *c*, in the upper part of the tube. Tubes of larger calibre, with water circulating below the boiling point, are likewise much used for warming large buildings.

Air and gases are very imperfect conductors. Heat appears to be propagated through them almost entirely by conveyance, the heated portions of air becoming lighter, and diffusing the heat through the mass in their ascent, as in liquids. Hence, in heating an apartment by hot air, the hot air should always be introduced at the floor or lowest part. The advantage of double windows for warmth depends in a great measure on the sheet of air confined between them, through which heat is very slowly transmitted. In the fur of animals, and in clothing, a quantity of air is detained among the loose fibres, which materially enhances their non-conducting property. In dry air, the human body can resist a temperature of 250° without inconvenience, provided it is not brought into contact with good conductors at the same time.

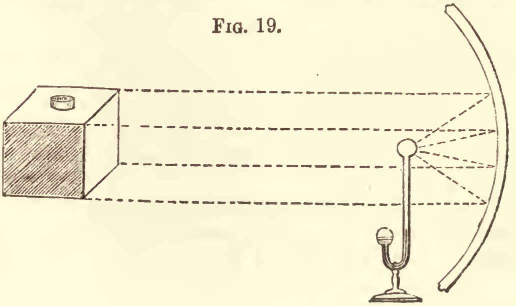
Radiation of Heat.—Heat is also emitted from the surface of bodies in the form of rays, which pass through a vacuum, air, and certain other transparent media, with the velocity of light. It is not necessary that a body be heated to a visible redness to enable it to discharge heat in this manner. Rays of heat, unaccompanied by light, continue to issue from a hot body through the whole process of its cooling, till it sinks to the actual temperature of the air or surrounding medium. The circumstance that bodies suspended in a perfect vacuum cool rapidly and completely, without the intervention of conduction, places the fact of the dissipation of heat by radiation, at low temperatures, beyond a doubt.

The most valuable observations which we possess on this subject, were published by Sir John Leslie, in his Essay on Heat, in 1804. Leslie proved that the rate of cooling of a hot body is more influenced by the state of its *surface* than by the nature of its *substance.* He filled a bright tin globe with hot water, and observed its rate of cooling in a room of which the air was undisturbed. A thermometer placed in the water cooled half way to the temperature of the apartment in 156 minutes. The experiment was repeated, after covering the globe with a thin coating of lamp-black. The whole now cooled to the same extent as in the first experiment, in 81 minutes; the rapidity of cooling being nearly doubled merely by this change of surface.

An experiment of Count Rumford is even more singular. Water, of the same temperature, was allowed to cool in two similar brass cylinders, one of which was covered by a tight investiture of linen, and the other left naked. The covered vessel cooled 10° in 36½ minutes, while the naked vessel required 55 minutes; or the covering of linen, like the coating of lamp-black, greatly expedited the cooling, instead of retarding the escape of heat, as might be expected. The cooling was accelerated in the same manner, when the cylinder was coated with black or white paint, or smoked by a candle.

In determining the radiating power of different surfaces, Leslie generally made use of square tin canisters, of which the surfaces were variously coated, and which he filled with hot water. Instead of watching

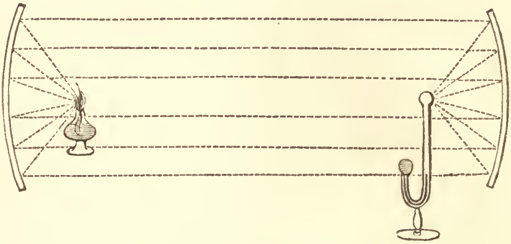
FIG. 19.



the rate of cooling, as in the experiments already mentioned, he presented the side of a canister, having its surface in any particular condition, to a concave metallic mirror, which concentrated the heat falling upon it into a focus, where the bulb of an air thermometer was placed to receive it, as represented in figure 19. The differential thermometer answered admirably for this purpose, as from its construction it is unaffected by the temperature of the room, while the slightest change in the temperature of the focal spot is immediately indicated by it.

Two metallic mirrors were occasionally used in conducting these experiments. The mirrors being arranged so as to face each other (fig. 20), with their principal axes in the same line; when a lighted lamp or hot canister is placed in the focus of one mirror, the incident rays are reflected by that mirror against the other, and collected in its focus.

Fig. 20.



The following table exhibits the relative radiating power of various substances with which the surface of the canister was coated, as indicated by the effect upon the differential thermometer:—

Lamp-black	100	Plumbago	75
Water by estimate	100+	Tarnished lead	45
Writing-paper	98	Clean lead	19
Sealing-wax	95	Iron, polished	15
Crown glass	90	Tin plate, gold, silver, copper	12

It thus appears that lamp-black radiates five times more of the heat of boiling water than clean lead, and eight times more than bright tin. The metals have the lowest radiating power, which arises from their brightness and smoothness. If allowed to tarnish, their radiating power is greatly increased. Thus the radiating power of lead with its surface tarnished is 45, and with its surface bright, only 19; but glass and porcelain radiate most powerfully, although their surface is smooth. When the actual radiating surface is metallic, it is not affected in a sensible manner by the substance under it. Thus, glass covered with gold-leaf possesses the radiating power of a bright metal.

It is placed beyond doubt, by the recent experiments of Prof. A. D. Bache, that the radiating power of any surface is not affected by its *colour*, at least in an appreciable degree. Hence, no particular colour of clothes can be recommended for superior warmth in winter. But the absorbent powers of bodies for the heat of the sun depend entirely upon their colour. (Journ. Franklin Inst., May and November, 1835.)

The faculty which different surfaces possess of *absorbing* or of *reflecting* heat radiated against them, is connected with their own radiating power. Those surfaces which radiate heat freely, such as lamp-black, glass, &c., also absorb a large proportion of the heat falling upon them, and reflect little of it; while surfaces which have a feeble radiating and absorbing faculty, such as the bright metals, reflect a large proportion, as they absorb little, and form the most powerful reflectors. So that the good absorbents are found at the top, and the good reflectors at the bottom of the preceding table. The efficiency of a reflector depending upon its low absorbing power, reflectors of glass are totally useless in conducting experiments upon radiant heat Metallic reflectors remain cold, although they collect much heat in their foci.

These laws of the radiation of heat admit of some practical applications. If we wish to retard, as much as possible, the cooling of a hot fluid or other substance, in what sort of vessel should we inclose it? In a metallic vessel, of which the surface is not dull and sooty, but clean and highly polished; for it has been observed, that hot water cools twice as fast in a tin globe of which the surface is covered with a thin coating of lamp-black, as in the same globe when the surface is bright and clean. Hence the advantage of bright metallic covers at table, and the superiority of metallic tea-pots over those of porcelain and stone-ware.

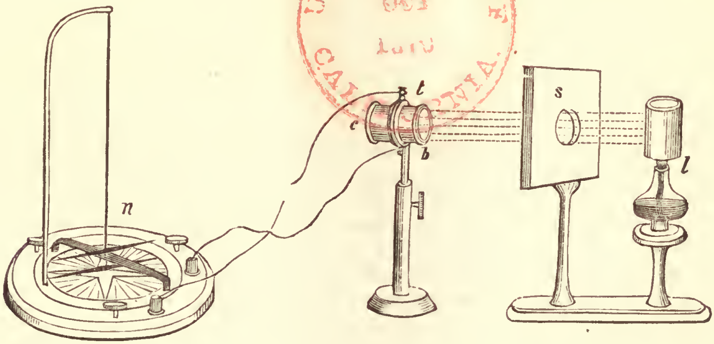
TRANSMISSION OF RADIANT HEAT THROUGH MEDIA, AND THE EFFECT OF SCREENS.

It has been shown by Dulong and Petit, that hot bodies radiate equally in all gases, or exactly as they radiate in a vacuum. Hot bodies certainly cool more rapidly in some gases than in others; but this is owing to the mobility and conducting powers of the gases being different.

Light of every colour, and from every source, is equally transmitted by all transparent bodies in the liquid or solid form; but this is not true of heat. The heat of the sun passes through any transparent body without loss; but of heat from terrestrial sources, a certain variable proportion only is allowed to pass, which increases as the temperature of the radiant body is elevated. Thus, it was observed by Delaroche that, from a body heated to 182°, only 1-40th of all the heat emitted passed through a glass screen: from a body at 346°, 1-16th of the whole; and from a body at 960°, so large a proportion as 1-4th appeared to pass through a glass screen. M. Melloni has, within the last few years, greatly extended our knowledge respecting the transmission of heat through media, in a series of the most profound researches.[1] In his experiments, he made use of the thermo-electric pile to detect changes of temperature; an instrument which, in his hands, exhibited a sensibility to the impressions of heat vastly greater than that of the most delicate mercurial or air thermometer.

His instrument, or the thermo-multiplier (fig. 21), consists of an arrangement of thirty pairs of bismuth and antimony bars contained in a brass cylinder, *t*, and having the wires from its poles connected with an extremely delicate magnetic galvanometer, *n*. The extremities of the bars at *b* being exposed to any source of radiant heat, such as the copper cylinder *d*, heated by the lamp *l*, while the temperature of the other extremities of the bars at *c* is not changed, an electric current passes through the wires from the poles of the pile, and causes the magnetic needle of the galvanometer to deflect. The force of the electric current increases in proportion to the difference of the temperatures of the two ends, *b* and *c*, that is, in

Fig. 21.



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[1] The complete series of Melloni's Memoirs is given in Taylor's Scientific Memoirs, Vols. I. and II.

proportion to the quantity of heat falling upon *b*; and the effect of this current upon the needle, or the deviation produced, is proportional to the force of the current, and consequently to the heat itself; at least, Melloni finds this correspondence to be exact through the whole arc, from zero to 20°, when the needle is truly astatic.

Melloni proved that heat, which has passed through one plate of glass, becomes less subject to absorption in passing through a second. Thus, of 1000 rays of heat from an oil flame, 451 rays being intercepted in passing through four plates of glass of equal thickness—

381	rays	were intercepted	by the first plate.
43	"	"	by the second.
18	"	"	by the third.
9	"	"	by the fourth.
451			

The rays appear to lose considerably when they enter the first layers of a transparent medium; but that portion of heat, which has forced its passage through the first layers, may penetrate to a great depth. Transparent liquids are found to be less penetrable to radiant heat than solids.

The capacity which bodies possess of transmitting heat does not depend upon their transparency; or bodies are not at all *transparent to heat* in the same proportion that they are transparent to light. Thus, plates of the following transparent minerals, having a common thickness of 0·1031 of an inch, allowed very different proportions of the heat from the flame of an argand oil-lamp to pass through them.

Of 100 incident rays there were transmitted:—

By Rock-salt	92	rays.
Mirror glass	62	"
Rock-crystal	62	"
Iceland spar	62	"
Rock-crystal, smoky and brown	57	"
Carbonate of lead	52	"
Sulphate of barytes	33	"
Emerald	29	"
Gypsum	20	"
Fluor spar	15	"
Citric acid	15	"
Rochelle salt	12	"
Alum	12	"
Sulphate of copper	0	"

A piece of smoky rock-crystal, so brown that the traces of letters on a printed page covered by it could not be seen, and which was fifty-eight times thicker than a transparent plate of alum, transmitted 19 rays, while the alum transmitted only 6. One substance, which is perfectly opaque, a kind of black glass used for the polarization of light by reflection, was found by Melloni to allow a considerable quantity of rays of heat to pass through it. He applied the term *diathermanous* to bodies which transmit heat, as *diaphanous* is applied to bodies which transmit light. Of all *diaphanous* or transparent bodies, water is in the least degree diathermanous. With the exception of the opaque glass referred to above, all diathermanous bodies belong also to the class of diaphanous bodies; for those kinds of metal, wood and marble, which totally obstruct the passage of light, obstruct that of heat also.

The proportion of heat from various sources which radiates through a plate of glass 1-50th of an inch in thickness, was observed by Melloni to be as follows:—

Of 100 rays	Transmitted.	Absorbed.
From the flame of an oil-lamp there were	54	46
" red hot platinum	37	63
" blackened copper, heated to 732° F.	12	88
" " " " 212°	0	100

But the power of transmission of rock-salt is the same for heat from all these sources, or for heat of all intensities; 92 per cent. of the incident heat being transmitted by that body, whether it be the heat radiated from the hand or from a bright argand lamp. Rock-salt stands alone in this respect among diathermanous bodies. This substance may be cut into lenses or prisms, and be used in concentrating heat of the very lowest intensity, or in decomposing it by double refraction, in the same manner as glass is employed with the light of the sun. Indeed, rock-salt has become quite invaluable in researches upon the transmission of heat.

It thus appears that a body at different temperatures emits different species of rays of heat, which may be sifted or separated from each other by passing them through certain transparent media. They are all emitted simultaneously, and in different proportions, by flame; but in heat from sources of lower intensity some of them are always absent. The calorific rays of the sun are chiefly of the kind which passes through glass; but Melloni shows that the other species are not altogether wanting. The rays of heat emitted by the sun and other luminous bodies are quite different rays from the rays of light with which they are accompanied.

Of the equilibrium of temperature. — When several bodies of various temperatures, some cold and some hot, are placed near each other, their temperatures gradually approximate, and, after a certain period has elapsed, they are found all to be of one and the same temperature. To account for the production and continuation of this equilibrium of temperature, it is necessary to assume that all bodies are at all times radiating heat in great abundance in all directions, although their temperature does not exceed or even falls below the temperature of the atmosphere. Hence, there is an incessant interchange of heat between neighbouring bodies; and a general equalization of temperature is produced when every object receives as much radiated heat as it emits.

This theory, which was first proposed by Prevost, of Geneva, enables us to account for the apparent radiation of cold. Cold, we know, is a negative quality, being merely the absence of heat, and cannot therefore be radiated. Yet, when a lump of ice is placed in the focus of a reflecting mirror, a thermometer in the focus of the opposite conjugate mirror is chilled. To account for this phenomenon we must remember that the temperature of the thermometer is stationary only so long as it receives as much heat as it radiates. It is in that state before the experiment is made with the ice; for the air or any object which may happen to be in the other focus is of the same temperature as the ball of the thermometer. But it is evident that the moment ice is introduced into one focus less heat will be sent from that to the other focus than was previously transmitted, and than is necessary to sustain the thermometer at a constant temperature. The thermometer ball, therefore, giving out as much heat as formerly, and receiving less in return, must fall in temperature. This is an experiment in which the thermometer ball is in fact the *hot body.*

The doctrine of the radiation of heat is happily applied to account for the deposition of *dew.* A considerable refrigeration of the surface of the ground below the temperature of the air resting upon it, amounting to 10 or 20 degrees, occurs every calm and clear night, and is caused by the radiation of heat from the earth (which is a good radiator) into empty space. Now, on becoming colder than the air above it, the ground will condense the moisture of the air in contact with it, and be covered with dew. For the air, however clear, is never destitute of watery vapour, and the quantity of vapour which air can retain depends upon its temperature; air at 52°, for instance, being capable of retaining 1-86th of its volume of vapour, while at 32° it can retain no more than 1-150th of its volume. The greatest difference between the temperature of the day and night takes place in spring and autumn, and these are the seasons in which the most abundant dews are deposited.

That the deposition of dew-drops depends entirely upon radiation is fully established by the following circumstances: — 1. It is on clear and calm nights only that dew is observed to fall. When the sky is overcast with clouds, no dew is formed; for then the heat which radiates from the earth is returned by the clouds above, and prevented from escaping into space; so that the ground never becomes colder than the air. 2. The slightest screen, such as a thin cambric handkerchief, stretched between pins, at the height of several inches above the ground, is sufficient to protect the objects below it from this chilling effect of radiation, and to prevent the formation of dew or of hoar-frost upon them. This fact was well known to gardeners, and they had long availed themselves of it in protecting their tender plants from frost, before the laws of the radiation of heat came to be explained. 3. Dr. Wells proved by numerous experiments that the quantity of dew which condenses on different objects exposed in the same circumstances is proportional to the radiating power of those substances. Thus, when a polished plate of metal and a quantity of wool are exposed together in favourable circumstances, scarcely a trace of dew is to be observed on the metal, while a large quantity condenses in the wool, the latter substance being incomparably the best radiator, and therefore falling to a much lower temperature than the metal.

The same theory has been applied to explain a process for making ice followed by the Indian natives near Calcutta. In that climate the temperature of the air rarely falls below 40° in the coldest nights; but the sky is clear, and a powerful radiation takes place from the surface of the ground. Hence, water contained in shallow pans imbedded in straw is often sheeted over with ice by a night's exposure. The water is certainly cooled by radiation from its surface, and not by evaporation; for the process succeeds best when the pans are placed in shallow trenches dug in the ground, an arrangement which retards evaporation; and no ice forms in windy weather, when evaporation is greatest.

The morning frosts of autumn are first felt in sequestered situations, as in ravines closed on all sides, or along the low courses of rivers, where the cooling of the earth's surface by radiation is in the least degree checked by the movement of the air over it. These are also the very situations upon which the sun's rays produce the greatest effect in summer.

Reverting again to the subject of conduction of heat through solid bodies, it may now be stated, that there is every reason to believe that heat is propagated, even in that case, in a manner not unlike radiation. Heat, in its passage through a bar of iron, is probably radiated from particle to particle; for the material atoms, of which the bar consists, are not supposed to be in absolute contact, although held near each other by a strong attraction. Radiation, as observed in air or a vacuum, may thus pass into conduction in solids, without any breach of continuity in the natural law to which heat in motion is subject. Baron Fourier proceeds upon such an hypothesis in his mathematical investigation of the law of cooling by conduction in solid bodies.[1]

We are now in a condition to advert with advantage to the equilibrium of the temperature of the earth. There can be no doubt of the existence, in this globe of ours, of a *central heat.* At a depth under the surface of the earth, not in general exceeding twenty feet, the thermometer is perfectly stationary, not being affected by the change of the seasons; but at greater depths the temperature progressively rises. M. Cordier, to whom we are indebted for a most profound investigation of this interesting subject, considers the two following conclusions to be established by all the observations on temperature which have been made at considerable depths. 1st. That below the stratum where the annual variations of the solar heat cease to be sensible, a notable increase of temperature takes place as we descend into the interior of the earth. 2dly. That a certain irregularity must be admitted in the distribution of the subterraneous heat, which occasions the progressive increase of temperature to vary at different places. Fifteen yards has been provisionally assumed as the average depth which

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[1] See a report by Professor Kelland, On the present state of our Theoretical and Experimental Knowledge of the Laws of the Conduction of Heat, in the Reports of the British Association for the Advancement of Science, for 1841, p. 1.

corresponds to an increase of one degree Fahrenheit. This is about 116 degrees for each mile. Admitting this rate of increase, we have at the depth of 30½ miles below the surface a temperature of 3500°, which would melt cast iron, and which is amply sufficient to melt the lavas, basalts, and other rocks, which have actually been erupted from below in a fluid state. But this central heat has long ceased to affect the surface of the earth. Fourier demonstrates, from the laws of conduction, that although the crust of the globe were of cast iron, heat would require myriads of years to be transmitted to the surface from a depth of 150 miles. But the crust of the globe is actually composed of materials greatly inferior to cast iron in conducting power. The temperature of the surface of the globe now depends upon the amount of heat which it receives from the sun, compared with the heat radiated away from its surface into free space. There is reason to believe that no material change has occurred in the quantity of heat received from the sun during the historical epoch. The radiation from the surface of the earth has its limit in the temperature of the planetary space in which it moves, which Fourier deduces, from calculation, to lie between —58° and —76°, and which Schwanberg, from a calculation on totally different principles, estimates at —58°.6; a close coincidence. This low temperature appears to be attained in the long absence of the sun during a polar winter, as Captain Parry found the thermometer to fall so low as —55° or —56° at Melville Island; and Captain Back has recorded a temperature observed on the North American continent so low as —70°.

FLUIDITY AS AN EFFECT OF HEAT.

One of the general effects of heat upon bodies has already been adverted to, namely its power of causing them to expand, which demanded our earliest attention, as it involves the principle of the thermometer. But heat, besides effecting changes in the bulk, is capable of effecting changes in the condition of bodies. Matter is presented to us in three very dissimilar conditions, or forms, namely, in the solid, liquid, and gaseous forms. It is believed that no body is restricted to any of these forms, but that the state of bodies depends entirely upon the temperature in which they are placed. In the lowest temperatures, they are all solid, in higher temperatures they are converted into liquids, and in the highest of all they become elastic gases. The particular temperatures at which bodies undergo these changes are exceedingly various, but they are always constant for the same body. The first effect, then, of heat on the state of bodies is the conversion of solids into liquids; or heat is the cause of fluidity.

Some substances, in liquefying, pass through an intermediate condition, in which it is difficult to say whether they are liquids or solids. Thus tallow, wax, and several other bodies, pass through every possible degree of softness before they attain complete fluidity. Such bodies, however, are in general mixtures of two or more substances, which crystallize imperfectly. But ice, and the great majority of bodies, pass immediately from the solid into the liquid state. The temperatures at which bodies undergo this change are exceedingly various.

	Melts at
Lead	594°
Bismuth	476
Tin	442
Sulphur	232
Wax	142
Spermaceti	112
Phosphorus	108
Tallow	92
Oil of anise	50
Olive oil	36°
Ice	32
Milk	30
Wines	20
Oil of turpentine	14
Mercury	—39
Liquid ammonia	—46
Ether	—47

If the bodies are in the fluid form, they freeze upon being cooled below the temperatures set against them.

It may be added, in reference to this table, first, that in certain circumstances liquids can be cooled down several degrees below their usual freezing point before they begin to congeal. Thus we may succeed, by taking certain precautions, in cooling a small quantity of water, in a glass tube, so low as the temperature 8°, or even as 5°, without its freezing; that is, 24 or 27 degrees under its proper freezing point 32°. The water must be cooled without the slightest agitation, and no sand or angular body be in contact with it; for the instant any solid body is dropped into water cooled below its freezing point, or a tremor is communicated to it, congelation commences, and the temperature of the liquid starts up to 32°. But, on the other hand, we cannot heat a solid the smallest fraction of a degree above its proper melting point, without occasioning liquefaction. Hence it is not the freezing of water, but the melting of ice, which takes place with rigorous constancy at 32° Fahrenheit.

All salts dissolved in water have the effect of lowering the freezing temperature of that liquid. Common culinary salt appears to depress this point lower than any other saline body; and the effect appears to be closely proportional to the quantity of salt in solution. A solution of 1 part of salt in 4 of water freezes at 4°; and sea-water, which contains 1-30th of its weight of salt, freezes at 28°.

But the principal fact to be adverted to in liquefaction is the disappearance of a large quantity of heat during the change. Heat pours into a body during its melting, without raising its temperature in the most minute degree. This heat, which enters the body and becomes insensible or latent, serves merely to melt the body. We are indebted to Dr. Black for this observation, which involves consequences of greater importance than any other announcement in the theory of heat.

Before Dr. Black's views were made known, fluidity was considered as produced by a very small addition to the quantity of heat which a body contains, when it is once heated up to its melting point. But if we attend to the manner in which ice and snow melt, when exposed to the air of a warm room, we can perceive that, however cold they may be at first, they are soon heated up to their melting point, and begin at their surface to be changed into water. Now, if the complete change of these bodies into water required only the farther addition of a very small quantity of heat, a mass of them, though of considerable size, ought all to be melted in a few minutes or seconds more, the heat continuing to be communicated from the air around. But masses of ice and snow melt with extreme slowness, especially if they be of a large size, as are those collections of ice and wreaths of snow that are formed in some places during winter. These, after they begin to melt, often require many weeks of warm weather, before they are totally dissolved into water. The slow manner in which ice melts in ice-houses is also familiarly known.

By examining what happens in these cases, it may easily be perceived that a very great quantity of heat must enter the melting ice, to form the water into which it is changed, and that the length of time necessary for the collection of so much heat from surrounding bodies is the reason of the slowness with which the ice is liquefied. When melting ice is suspended in warm air, the entrance of heat into it is made sensible by a stream of cold air descending constantly from the ice, which may be perceived by the hand. It is, therefore, evident that the melting ice receives heat very fast; but the only effect of this heat is to change it into water, which is not in the least sensibly warmer than the ice was before. A thermometer applied to the drops or small streams of water as they come immediately from the melting ice, will point to the same degree as when applied to the ice itself. A great quantity of the heat, therefore, which enters into the melting ice, has no other effect than that of giving it fluidity. The heat appears to be absorbed or concealed within the water, and cannot be detected by the thermometer.

When ice is melted by means of warm water, this absorption of heat is made exceedingly obvious. Thus, on mixing a pound of water at 172° with a pound of snow at 32°, the snow is all melted, and the mixture is two pounds of water of the temperature of 32°. In being cooled down from 172° to 32°, the hot water loses 140 degrees of heat, which convert the snow into water, indeed, but produce no rise of temperature in the mixture above the 32 degrees originally possessed by the snow.

Dr. Black proved that the heat which disappears in this manner is not extinguished or destroyed, but remains latent in the water so long as it is fluid, and is extricated again when it freezes.

In water that has been cooled below its usual freezing point, when the congelation is once determined, quantities of icy spiculæ are produced in proportion to the depression of temperature, whilst at the same instant the temperature of ice and water starts up to 32°. The heat which thus appears was previously latent in that portion of the water which is frozen. The same disengagement of latent heat may be conveniently illustrated by means of a supersaturated solution of sulphate of soda, formed by dissolving, at a high temperature, three pounds of the salt in two pounds of water. When this liquid is allowed to cool undisturbed, and with a stratum of oil on its surface, it remains fluid, although containing a much greater quantity of salt in solution than the water could dissolve at the temperature to which it has fallen. But the suspended congelation of the salt being determined by the introduction of any solid substance into the solution, the temperature then often rises 30 and even 40 degrees, while crystals of sulphate of soda shoot rapidly through the liquid.

Wax, tallow, sulphur, and all other solid bodies, are melted in the same manner as water, by the assumption of a certain dose of heat. The latent heat which the following substances possess in the fluid form was, with the exception of water, determined by Dr. Irvine.

	Latent heat.
Water	142 degrees.[1]
Sulphur	145 "
Lead	162 "
Bees'-wax	175 "
Zinc	493 "
Tin	500 "
Bismuth	550 "

Even in the solid form certain bodies admit of a variation in their structure and properties from the assumption or loss of latent heat. Dr. Black made it appear probable that metals owe their malleability and ductility to a quantity of latent heat combined with them. When hammered they become hot from the disengagement of this heat, and at the same time become brittle. Their malleability is restored by heating them again in a furnace. Sugar, it is well known, may exist as a transparent and colourless body, with the physical properties of glass, or as a white and opaque, because a granular or crystalline mass. The transition from the glassy to the granular state is attended by a very remarkable evolution of heat, which appears to have escaped the notice of scientific men. If melted sugar be allowed to cool to about 100°, and then, while it is still soft and viscid, be rapidly and frequently extended and doubled up, till at last it consists of threads, as in drawn sugar, the temperature of the mass quickly rises so as to become insupportable to the hand. After this liberation of heat, the sugar on again cooling is no longer a glass, but consists of minute crystalline grains, and has a pearly lustre. The same change may occur in a gradual manner, as when a clear stick of barley-sugar becomes white and opaque in the atmosphere; but then we have no means of observing the escape of the latent heat on which the change depends. It may be inferred that glass itself, like transparent barley-sugar, owes its peculiar constitution and properties to the permanent retention of a certain quantity of latent heat. Of this heat glass can be deprived by keeping it long in a soft state; it then becomes granular, and, passing into the condition of Reaumur's porcelain, loses all the characters of glass.

It is not unlikely that the *dimorphism* of a body, or its property to assume two different crystalline forms, may likewise depend upon the retention of a certain

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[1] De la Provostaye and Regnault, Annales de Chimie, &c., 3 sér. t 8, p. 1.

quantity of latent heat by the body in the one form, and not in the other. Thus, sulphur assumes two forms, one on cooling from a state of fusion by heat, another in crystallizing at a lower temperature, and probably with the retention of less latent heat, from a solution of sulphuret of carbon. In charcoal and plumbago, again, we have carbon which has assumed the solid form at a high temperature, and possibly with the fixation of a quantity of latent heat which does not exist in the diamond, another form of the same body.

When a solid body is melted by the intervention of some affinity, without heat being applied to it, cold is generally produced. Thus, most salts occasion a reduction of temperature, in the act of dissolving in water, which requires them to become fluid. Nitre, for instance, cools the water in which it is dissolved 15 or 18 degrees. A mixture of five parts of sal ammoniac and five of nitre, both finely powdered, dissolved in nineteen parts of water, may reduce its temperature from 50° to 10°, or considerably below the freezing point of pure water. These salts are necessitated, by their affinity for water, to dissolve when mixed with it, and to become fluid, a change which implies the assumption of latent heat. Most of our artificial processes for producing cold are founded upon this disappearance of heat during liquefaction. A very convenient process for freezing a little water, without the use of ice, is to drench finely powdered sulphate of soda with the undiluted hydrochloric acid of the shops. The salt dissolves to a greater extent in this acid than in water, and the temperature may sink from 50° to 0°. The vessel in which the mixture is made becomes covered with hoar frost, and water in a tube immersed in the mixture is speedily frozen.

The same affinity between salts and water may be taken advantage of to cause the liquefaction of ice. On mixing snow with a third of its weight of salt, the snow is instantly melted, and the temperature sinks nearly to 0°. It was in this way that Fahrenheit is supposed to have obtained the zero of his scale. Ices for the table are always made in summer by mixing roughly pounded ice and salt together, and immersing the cream, or other liquid to be frozen, contained in a thin metallic pan, in the cold brine which is produced by the melting of the ice.

The liquefaction of snow by means of the salt, chloride of calcium, occasions a still greater degree of cold. To prepare this salt, marble or chalk is dissolved in hydrochloric acid, and the solution evaporated by a temperature not exceeding 300°. It should be stirred, as it becomes dry at this temperature; and is obtained in a crystalline powder, being the combination of chloride of calcium with two atoms of water. When three parts of this salt are mixed with two of dry snow, the temperature is reduced from 32° to —50°. In attempting to freeze mercury by means of this mixture, it is advisable to make use of not less than three or four pounds of the materials. When the materials are divided, and the mercury is first cooled considerably by one portion, it rarely fails in being frozen when transferred into another portion of the mixture. For producing still more intense degrees of cold, the evaporation of highly volatile liquids, of liquid carbonic acid, for instance, affords the most efficient means.

VAPORIZATION.

We have now to consider the second general effect of heat—Vaporization, or the conversion of solids and liquids into vapour. Vapours, of which steam is the most familiar to us, are light, expansible, and generally invisible gases, resembling air completely in their mechanical properties, while they exist, but subject to be condensed into liquids or solids by cold. Water undergoes a great expansion when converted into steam, a cubic inch of water becoming, in ordinary circumstances, a cubic foot of steam; or, more strictly, one cubic inch of water, when converted into steam, expands into 1694 cubic inches.

This change, like fluidity, is produced by the addition of heat to the body which undergoes it. But a much larger quantity of heat enters into vapours than into liquids, into steam than into water. If, over a steady fire, a certain quantity of ice-cold water requires one hour to bring it to the boiling point, it will require a continuance of the same heat for five hours more to boil it off entirely. Yet liquids do not become hotter after they begin to boil, however long, or with whatever violence the boiling is continued: for if a thermometer be plunged into water, and the point marked where it stands at the beginning of the boiling, it will be found to rise no higher, although the boiling be continued for a long time.

This fact is of importance in domestic economy, particularly in cookery; and attention to it would save much fuel. Soups, &c., made to boil in a gentle way, by the application of a moderate heat, are just as hot as when they are made to boil on a strong fire with the greatest violence; when water in a copper is once brought to the boiling point, the fire may be reduced, as having no further effect in raising its temperature, and a moderate heat being sufficient to preserve it.

The steam from boiling water, when examined by the thermometer, is found to be no hotter than the water itself. What, then, becomes of all the heat which is communicated to the water, since it is neither indicated in the steam nor in the water? It enters into the water, and converts it into steam, without raising its temperature. As much heat disappears as is capable of raising the temperature of the portion of water converted into steam 1000 degrees, or, what is the same thing, as would raise the temperature of one thousand times as much water by one degree. This is now generally assumed to be the amount of the latent heat of steam. Dr. Black found it to be about 960 degrees, Mr. Watt 940 degrees, and Lavoisier rather more than 1000 degrees.

Several circumstances may be remarked during the occurrence of this change in water. On heating water gradually in a vessel, we first observe minute bubbles to form in the liquid, and rise through it, which consist of air. As the temperature increases, larger bubbles are formed at the bottom of the vessel, which rise a little way in the liquid, and then contract and disappear, producing a hissing or simmering sound. But, as the heating goes on, these bubbles, which are steam, rise higher and higher in the liquid, till at last they reach its surface and escape, producing a bubbling agitation, or the phenomenon of *ebullition.* The whole process of boiling is beautifully seen in a glass vessel. It will be remarked that steam itself is invisible; it only appears when condensed again into minute drops of water by mixing with the cold air.

It was first observed by Gay-Lussac, that liquids are converted more easily into vapour when in contact with angular and uneven surfaces, than when the surfaces which they touch are smooth and polished. He also remarked that water boils at a temperature two degrees higher in glass than in metal; so that if into water, in a glass flask, which has ceased to boil, a twisted piece of cold iron be dropped, the boiling is resumed: it is only in vessels of metal that the boiling point is regular, and should be taken in graduating thermometers. It has been remarked by Mr. Scrymgeour, of Glasgow, that if oil be present with water, the boiling point of the water is raised a few degrees, in any kind of vessel. A much greater elevation of the boiling point has been observed by M. Marcet, (Ann. de Chimie, &c., 3 sér. t. 5, p. 449), in a glass flask, having its inner surface coated with a thin film of shellac, in which the temperature often rises to 221°, or even higher, before a burst of vapour occurs; it then sinks a few degrees, after which it rises again.[1] The reason why water in these circumstances does not pass into vapour at its usual boiling point, is not distinctly understood. The water appears to be in a precarious state of equilibrium, as in the other analogous case, when cooled with caution in a smooth glass vessel considerably under its usual freezing point. The introduction of an angular body into the water is sufficient, in either instance, to induce the sus-

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[1] The author has quoted incorrectly the results of Marcet's experiments, as referred to above. The statements made, are to the effect that in glass vessels deprived of all foreign matter on their surface, a marked elevation of the temperature of ebullition may be obtained, distilled water not boiling below 105° C. (221° F.); but in vessels coated with shellac or sulphur, this temperature is inferior by some tenths of a degree to that in metal vessels. — R. B

pended change. The same irregular deviation of the boiling point in glass vessels takes place in other liquids as well as water, and in some of them to a much greater extent.

There is a curious circumstance in regard to boiling, which is a matter of common observation in some shape or other. When a little water (a few drops) is thrown into a metallic cup considerably above the boiling point of water, the liquid assumes a spheroidal form, and rolls about the cup like melted crystal, without visible ebullition, being only slowly dissipated. The cause of the phenomenon appears to be this. Water exhibits an attraction for the surface of almost all solids at low temperatures, and wets them. Fluid mercury exhibits the opposite property, or a repulsion for most surfaces. The attraction of water for surfaces brings it into the closest contact with them, and greatly promotes the communication of heat by a heated vessel to the water contained in it. But heat appears to develope a repulsive power in bodies, and it is probable that above a particular temperature the heated metal no longer possesses this attraction for water. The water, not being attracted to the surface of the hot metal, and induced to spread over it, is not rapidly heated, and therefore boils off slowly. A rude method of judging of the degree of heat is founded on the same principle, and is seen familiarly exemplified in the laundry. The heat of the smoothing iron is judged of by its effects upon a drop of saliva let fall upon it. If the drop do not boil, but run along the surface of the metal, the iron is considered sufficiently hot; but if the drop adheres and is rapidly dissipated, the temperature is considered low.

The spheroidal ebullition of liquids, which was first examined by Leidenfrost, in 1756, has lately received from M. Boutigny some striking experimental illustrations (Annales de Chimie, &c., 3 sér. t. ix. p. 350; et t. xi. p. 16). He has observed that water may pass into spheroidal ebullition at any temperature above 340°, and remain in that state till the temperature falls to 288°; then it moistens the metallic capsule in which the experiment is made, and evaporates rapidly. The corresponding temperatures at which alcohol and ether pass into the spheroidal form in a heated capsule were found to be proportional to their points of ebullition; the temperature for the first being 273°, and for the second 142°. The ball of a thermometer being plunged in liquids while in the spheroidal state, indicated the temperatures — in water, of 205·7°; in absolute alcohol, of 167·9°; in ether, 93·6°; in hydrochloric ether, 50·9°; in sulphurous acid, 13·1°; which are all several degrees below the ordinary temperatures of ebullition of these liquids. When distilled water is allowed to fall drop by drop into sulphurous acid in the spheroidal state, the water is immediately congealed into a spongy mass of ice, even when the containing capsule is visibly red-hot.

The temperature at which any liquid boils is not fixed (like the melting point of solids), but depends entirely upon a particular circumstance,—the degree of pressure to which the liquid is at the time subject. Liquids are in general subject to the pressure of the atmosphere; for although the air is an exceedingly light substance, being 815 times lighter than water, yet by reason of its great quantity and height, it comes to weigh with considerable force upon the earth. This is called the atmospheric pressure, and amounts to about fifteen pounds upon each square inch of surface. The force with which air presses upon a man of ordinary size has been estimated at fifty tons; yet, from all the cavities of the animal frame being filled with equally elastic air, we support this great pressure without being sensible of it; indeed, we should suffer the greatest inconvenience from its sudden removal. Now the pressure of the atmosphere is not always the same at the same place, but is found by the barometer to vary within the limits of one-tenth of the whole pressure. This difference affects the boiling point to the extent of 4½ degrees. Thus, when the height of the mercury in the barometer is expressed by the numbers in the first column, water boils at the temperatures placed against them in the second column.

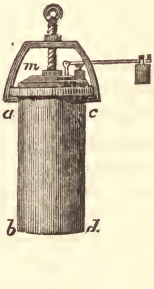
Barometer in inches of mercury.	Water boils.
27·74	208°
28·29	209
28·84	210
29·41	211
29·92	212
30·6	213

On this account the pressure of the atmosphere must be attended to in fixing the boiling point of water on thermometers. Water boils at 212° only when the pressure of the atmosphere is equivalent to a column of 29·92 inches of mercury.

The pressure of the atmosphere will be greatest at the level of the sea, and will diminish as we ascend to any height above it, for then we have less of the atmosphere above and pressing upon us, part of it being below us. Hence, water boils on the tops of mountains at a considerably lower temperature than at their bases. On the top of Mont Blanc, which is the pinnacle of Europe, water was observed by Saussure to boil at 184°. In deep pits, on the other hand, water requires a higher temperature to boil it than at the surface of the earth. An instrument has been constructed for ascertaining the heights of mountains on this principle. It consists essentially of a thermometer, graduated with great care about the boiling point of water, by means of which the temperature at which water boils at different altitudes can be ascertained with minute accuracy. A difference of one degree of temperature is occasioned by an ascent of about 550 feet, and the depression of the boiling point is accurately proportional to the elevation above the earth's surface, according to the observations of Prof. Forbes (Edinburgh Phil. Trans. xv. 409).[1]

When the pressure on liquids is removed by artificial means, they boil at greatly reduced temperatures. This may be done by placing them under the receiver of an air-pump, and exhausting. When the whole air is withdrawn, liquids in general boil at about 145° under the temperature which they require to make them boil when subject to the atmospheric pressure. In a good vacuum water will boil at 67°. This fact is also illustrated by a simple experiment which any one may perform. A flask, containing boiling water, is closed with a cork, while the upper part is filled with steam. The boiling in the flask may be renewed by plunging it into cold water; and the colder the water the brisker will the ebullition become. But the boiling is instantly checked by removing the flask from the cold water and immersing it in very hot water. On corking the flask the ebullition ceased from the pressure exerted by the confined steam upon the surface of the water; but on plunging the flask into cold water, the steam was condensed, and the water began to boil under the reduced pressure. On removing the flask to the hot water, the steam above ceased to be condensed, and by its pressure stopped the boiling. On the other hand, in a Papin's digester, which is a tight and strong kettle with a safety valve, water may be raised to 3 or 400° without ebullition: but the instant that this great pressure is removed, the boiling commences with prodigious violence.

Fig. 22.



The facility with which liquids boil under reduced pressure is frequently taken advantage of in the arts, in concentrating liquors which would be injured in flavour or colour by the heat necessary to boil them under the pressure of the atmosphere. Mr. Howard applied this principle in concentrating the syrup of sugar, which is apt to be browned when made to boil under the usual pressure. He thus boiled syrup at 150°, applying heat to it in a pan covered by an air-tight lid, and pumping off the air and steam from the upper part

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[1] For the most recent minute determinations of the boiling point of water, under variations of atmospheric pressure, see the memoir of M. Regnault; Ann. de Chimie, &c., 3 série, t. xiv. p. 196. A simple portable apparatus for the experiment is also described there.

of the pan by means of a steam-engine. This was the most essential part of his patent process, by which nearly the whole of the loaf sugar consumed in this country has been manufactured for many years.

In the same apparatus vegetable infusions may be inspissated, or reduced to the state of extracts, for medical purposes, with great advantage. When an extract is prepared in the ordinary way, by boiling down an infusion or expressed juice in an open vessel under atmospheric pressure, a considerable and variable proportion of the active principle is always destroyed by the high temperature and exposure to the air. But the extract is not injured when the infusion or juice is evaporated at a low temperature, and without access of air, and is generally found to be a more active medicine.

The temperatures at which different liquids are converted into vapour are exceedingly various; but other things remaining the same, the boiling temperature is constant for any particular liquid. The following table exhibits the boiling points of a few liquids, in which that point has been determined with precision: —

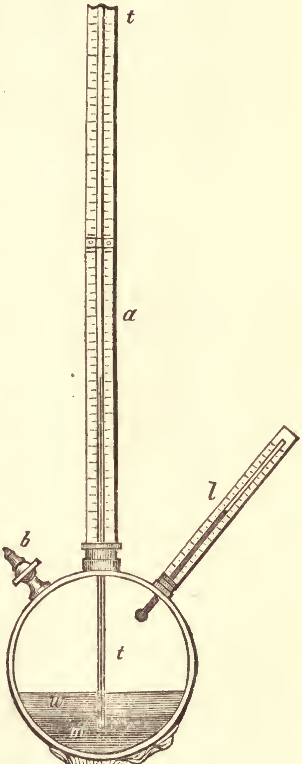
	Boiling point.
Hydrochloric ether	52°
Ether	96
Sulphuret of carbon	118
Ammonia (sp. gr. 0·945)	140
Alcohol	173
Water	212
Nitric acid (sp. g. 1·42)	248
Crystallized chloride of calcium	302
Oil of turpentine	314
Naphtha	320
Phosphorus	554
Sulphuric acid (sp. gr. 1·843)	620
Whale oil	630
Mercury	662

The boiling point of water is uniformly elevated by the solution of salts in the fluid; but much more so by some salts than others. Tables have been constructed of the boiling points of saline liquors, which are of useful application when it is wished to maintain a steady temperature somewhat above 212°. Thus, water saturated with common salt (100 water to 30 salt), boils at 224°; saturated with nitrate of potash (100 water to 74 salt), it boils at 238°; saturated cold with chloride of calcium, at 264°.

When steam from water is confined, it increases in temperature, and acquires great force; and the experiment can only be performed with safety in a boiler possessed of a safety-valve. This is a small lid in the upper part of the boiler, properly loaded, according to the force of the steam to be generated. The steam of boiling water occasions a severe scald, if allowed to condense upon the body. But when steam from water under pressure, or "high pressure" steam, which may be of a much higher temperature than boiling water, issues into the air, the hand may be directly exposed to it with impunity; and a thermometer placed in it shows that its temperature is greatly below that of boiling water. This singular property of high pressure steam is connected with the great expansion which it undergoes on escaping into the air from the vessel in which it was confined; elastic bodies having a tendency, when escaping from a state of compression, to fly asunder, not only to their original dimensions, but beyond them. The steam is greatly expanded, and at the same time mixed with air, which prevents it from afterwards collapsing. Now, after being incorporated with several times its bulk of air, steam is not easily condensed, but becomes low-pressure steam, and may have its condensing point reduced from above 212° to 120° or 130°. Hence the heat which it is capable of communicating, while condensing upon the hand held in it, is of much less intensity than that of ordinary steam, and inadequate to occasion scalding.

Steam, when heated by itself, apart from the liquid which produced it, does not possess a greater elasticity than an equal bulk of air confined and heated to the same degree, and may be heated to the temperature at which the containing vessel becomes red hot, without acquiring great elastic force. But if water be present, then more and more steam continues to rise, adding its elastic force to that of the vapour previously existing, so that the pressure becomes excessive.

FIG. 23.



The elastic force of steam at temperatures above 212° is determined by heating water in a stout globular vessel containing mercury, *m*, (see fig. 23,) and water, *w*, and having a long glass tube, *t t*, screwed into it, open at both ends, and dipping into the mercury, with a scale, *a*, divided into inches, applied to it. The globular vessel has two other openings, into one of which a stopcock, *b*, is screwed, and into the other thermometer, *l*, having its bulb within the globe. The water is boiled in this vessel for some time, with the stopcock open so as to expel all the air. On shutting the stopcock, and continuing the heat, the temperature of the interior, as indicated by the thermometer, now rises above 212°, at which it was stationary while the steam generated was allowed to escape. The steam in the upper part of the globe becomes denser, more and more steam being produced, and forces the mercury to ascend in the gauge tube, *t*, to a height proportional to the elastic force of the steam. The height of the mercurial column is taken to express the elastic force or pressure of the steam produced at any particular temperature above 212°. The weight of the atmosphere itself is equivalent to a column of mercury of 30 inches, and this pressure has been overcome by the steam at 212°, before it began to act upon the mercurial gauge. For every thirty inches that the mercury is forced up in the gauge tube by the steam, it is said to have the pressure or elastic force of another atmosphere. Thus, when the mercury in the tube stands at thirty inches, the steam is said to be of two atmospheres; at 45 inches, of two and a half atmospheres; at 60 inches, of three atmospheres, and so on.

Experiments have been made on the elastic force of steam by Professor Robison, Mr. Southern, Mr. Watt, and others; but all preceding results have been superseded by those of a commission of the French Academy, consisting of MM. Dulong and Arago, appointed by the French government to investigate the subject, from its importance in connexion with the steam engine (Annales de Chimie, &c. 2 sér. t. xliii. p. 74). Their results, which are expressed in the following table, were obtained by experiment, up to a pressure of 25 atmospheres. The higher pressures were calculated by extending the progression observed at lower temperatures: —

Elasticity of Steam taking Atmospheric Pressure as Unity.	Temp. Fahr.
1	212.0
1½	233.96
2	250.52
2½	263.84
3	275.18
3½	285.08
4	293.72
4½	300.28
5	307.5
5½	314.24
6	320.36
6½	326.26
7	331.20
7½	336.50
8	341.78
9	350.78
10	358.28
11	366.85
12	374.00
13	386.66
14	386.94
15	392.46
16	398.48
17	403 82
18	408.92
19	413.78
20	418.46
21	422.96
22	427.28
23	431.42
24	435.56
25	439.34
30	457.16
35	472.73
40	486.59
45	499.14
50	510.60

Some curious experiments were made by M. Cagniard de la Tour on the vapour from various liquids at very high temperatures, and under great pressures. He filled a small glass tube in part with ether, alcohol, or water, and sealed it hermetically. The tube was then exposed to heat, till the liquid passed entirely into vapour. Ether became gaseous in a space scarcely double its volume at a temperature of 320°, and the vapour exerted a pressure of no more than 38 atmospheres. Alcohol became gaseous in a space about thrice its volume at the temperature of 404½°, with a pressure of about 139 atmospheres. Water acted chemically on the glass, and broke it; but adding a little carbonate of soda to it, the water became gaseous in a space four times its volume at the temperature at which zinc melts, or about 648°. These results are singular, in so far as the pressure or elastic force of the vapours proves to be much smaller than that which corresponds with their calculated density. It thus appears that highly compressed vapours lose a portion of their elasticity, or yield more to a certain pressure than air, by calculation, would do.

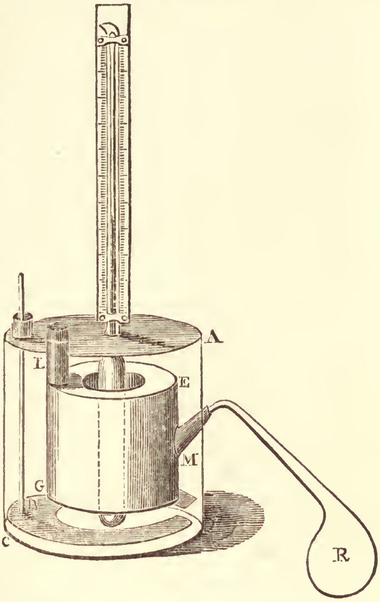
A measure is obtained of the quantity of latent heat in steam by observing the degree to which it heats up a mass of water when condensed in it. Cold water is easily made to boil by placing the open end of a pipe from a steam-boiler in it, and causing the steam to blow through it for a sufficient time. If a measured quantity of water at 32°, amounting to 11 cubic inches, is heated up to 212° in this manner, it is found that the volume is increased to 13 cubic inches by the condensed steam. Consequently, 11 cubic inches of water are heated up from 32° to 212°, or one hundred and eighty degrees, by 2 cubic inches of water in the form of steam. But if, for comparison, 2 cubic inches of boiling hot water be substituted for the steam, and added to 11 cubic inches of cold water, the temperature of the latter is raised no more than about twenty-eight degrees. In both experiments, however, the temperature of the steam, and of the boiling water added, was the same, or 212°; the difference of their heating effects depends entirely upon the latent heat which the former possesses, in addition to its sensible temperature, and abandons to the cold water on condensing.

In the condensing experiment 2 cubic inches of water in the form of steam raised the temperature of 11 cubic inches of water one hundred and eighty degrees, or 1 of steam raised the temperature of 5½ of water to that amount. As it follows that one part of steam would heat one part of water, 5½ times 180, or 990 degrees, it appears that steam possesses as much heat latent as might raise its own temperature to that amount on becoming sensible.

The latest, and probably most exact, determinations which we possess of the latent heat of the vapours of water, and other liquids, are those of M. Brix, of

Berlin, (Poggendorff's Annalen, lv.) He employed the apparatus represented in Fig. 24. The refrigeratory to contain the cold condensing water consists of a cylindrical vessel, A C, 3 inches in diameter and 3 inches deep. The steam from a small retort R does not pass directly into the water of the refrigeratory, but is conveyed by the spout M into an inner hollow cylinder E G, of a ring-formed basis, which has an opening into the atmosphere by the tube L, by which the air it contains finds vent on the arrival of the vapour. The condensing water is agitated by means of a thin disc of metal B, attached to a vertical rod, the upper end of which passes through the cover of the refrigeratory. A known quantity of cold water being introduced into this refrigeratory, its temperature is accurately observed by the including thermometer. In conducting the experiments it was arranged that the temperature of the condensing water should at first be a few degrees below that of the atmosphere, and vapour was thrown into the inner receiver by boiling a weighed portion of liquid in R, till the temperature of the condensing water rose as many degrees above that point. The weight of liquid distilled is then found by weighing the retort R with what remains in it, and ascertaining the loss; and the latent heat calculated by increasing the rise of temperature observed in the refrigeratory, in the same proportion as the weight of the condensing water in the refrigeratory exceeds that of the liquid distilled from the retort.

Fig. 24.



The following are the mean results which M. Brix obtained by this method, several experiments being made upon each liquid:—

Equal weights.	Latent heat of vapour.
Water	972 degrees.
Alcohol	385.2 “
Ether	162 “
Oil of turpentine	133.2 “
Oil of lemons	144 “

Despretz, who at an earlier period had also made very careful experiments on several of the same liquids, gave the following estimations of latent heat:—

Equal weights.	Latent heat of vapour.
Water	955.8 degrees.
Alcohol	374.4 “
Ether	174.6 “
Oil of turpentine	138.6 “

Dulong obtained for the latent heat of the vapour of water 977.4 degrees.

It is to be further remarked, that equal weights of these liquids yield very different volumes of vapour, owing to the different specific gravities of the latter; and the densest vapours appear to have generally the least latent heat. According to the table of M. Brix, the latent heat of the vapour of water is 972 degrees, while that of the vapour of alcohol is 385 degrees: or water-vapour has for equal weights about 2.5 times more latent heat than alcohol-vapour. The specific gravity of alcohol-vapour, on the other hand, is about 2.5 times greater than that of water-vapour, taking the former at 1589.4, and the latter at 622; consequently, equal volumes of these two vapours possess equal quantities of latent heat.

If the latent heat of different vapours be proportional to their volume, as these numbers seem to indicate, the same bulk of vapour will be produced from all liquids with the same expenditure of heat; and hence there can be no advantage in substituting any other liquid for water, as a source of vapour, in the steam-engine.

The latent heat of the vapour of water itself increases with its rarity at low temperatures, and diminishes with its increasing density at high temperatures. Water may easily be made to boil in a vacuum at the temperature of 100°, but the steam produced is much more expanded and rare than that produced at 212°, and has a greater latent heat. Hence there is no fuel saved by distilling in vacuo. It has been shown, by Mr. Sharpe, of Manchester, that whatever be the temperature of steam, from 212° upwards, if the same weight of it be condensed by water, the temperature of the water will always be raised the same number of degrees; or the latent and sensible heat of steam, added together, amount to a constant quantity. We may hence deduce a simple rule for ascertaining the latent heat of steam at any particular temperature. The sensible heat of steam at 212° may be assumed at 212 degrees, neglecting the heat which it has below zero Fahrenheit, and the latent heat of such steam is 972 degrees, of which the sum is 1184 degrees. To calculate the latent heat of steam at any particular temperature above 212°, subtract the sensible heat from this constant number 1184. Thus the latent heat of steam at 300° is 1184—300, or 884 degrees. The same relation between the latent and sensible heat of vapour appears to exist at temperatures below 212°, and the latent heat of vapour, below that temperature, may therefore be calculated by the same rule.*

Temperature.	Latent heat of Equal Weights of Steam.
0°	1184 degrees.
32°	1152 "
100°	1084 "
150°	1034 "
212°	972 "
250°	934 "

The latent heat of other vapours, such as that of alcohol, ether, and oil of turpentine, has been found by Despretz to vary according to the same law.

From the large quantity of heat which steam possesses, and the facility with which it imparts it to bodies colder than itself, it is much used as a vehicle for the communication of heat. The temperature of bodies heated by it can never be raised above 212°; so that it is much preferable to an open fire for heating extracts and organic substances, all danger of empyreuma being avoided. When applied to the cooking of food, the steam is generally conveyed into a shallow tin box, in the upper surface of which are cut several round apertures, of such sizes as admit exactly the pans with the materials to be heated. The pans are thus surrounded by steam, which condenses upon them with great rapidity, till their temperature rises to within a degree or two of 212°. For some purposes, a pan containing the matters to be heated is placed within another and similar larger one, and steam admitted between the two vessels. Manufactured goods also are often dried by passing them once over a series of metallic cylinders, or of square boxes filled with steam. Factories are now very generally heated by steam, conveyed through them in cast-iron pipes. It has been found by practice that the boiler to produce steam for this purpose must have one cubic foot of capacity for every 2,000 cubic feet of space to be heated to a temperature of 70° or 80°; and that of the conducting steam pipe, one square foot of surface must be exposed for every 200 cubic feet of space to be heated.

The expansion of water into steam is used as a moving power in the steam engine. The application is made upon two different principles, both of which may

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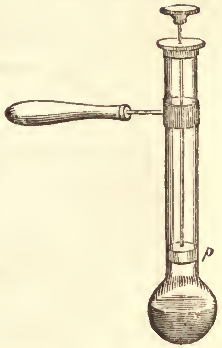
* [*See Supplement*, p. 643.]

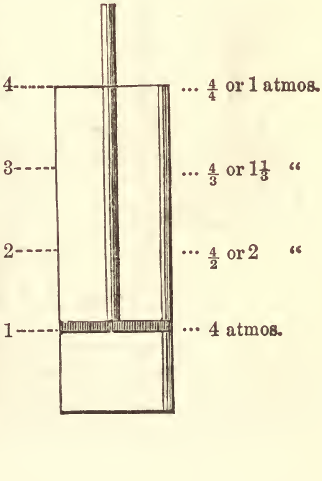
Fig. 25.



be illustrated by the little instrument depicted on the margin. It consists of a glass tube, about an inch in diameter, slightly expanded into a bulbous form at one extremity, and open at the other (fig. 25); a piston is made, by twisting tow about the end of a piece of straight wire, which must be fitted tightly in the tube by the use of grease. Upon heating a little water in the bulb below piston *p*, steam is generated, which raises the piston to the top of the cylinder. Here the simple elastic form of the steam is the moving power; and in this manner steam is employed in the high pressure engine. The greater the load upon the piston, and the more the steam is confined, the greater does its elastic force become. Again: the piston being at the top of the cylinder, if we condense the steam with which the cylinder is filled, by plunging the bulb in cold water, a vacuum is produced below the piston, which is now forced down to the bottom of the cylinder by the pressure of the atmosphere. In this second part of the experiment, the power is acquired by the condensation of the steam, or the production of a vacuum; and this is the principle of the common condensing engine. In the first efficient form of the condensing engine (that of Newcomen) the steam was condensed by injecting a little cold water below the piston, which then descended, from the pressure of the atmosphere upon its upper surface, exactly as in the instrument. But Mr. Watt introduced two capital improvements into the construction of the condensing engine; the first was, the admitting steam, instead of atmospheric air, to press down the piston through the vacuous cylinder, which steam itself could afterwards be condensed, and a vacuum produced above the piston, of which the same advantage might be taken as of the vacuum below the piston. The second was, the effecting the condensation of the steam, not in the cylinder itself, which was thereby greatly cooled, and occasioned the waste of much steam in being heated again at every stroke; but in a separate air-tight chamber, called the condenser, which kept cool and vacuous. Into this condenser the steam is allowed to escape from above and from below the piston alternately, and a vacuum is obtained without ever reducing the temperature of the cylinder below 212°.

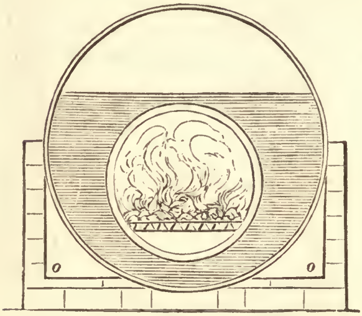
A third improvement in the employment of steam as a moving power consists in using it *expansively;* a mode of application which will be best understood by being explained in a particular case. Let it be supposed that a piston, loaded with one ton, is raised four feet by filling the cylinder in which it moves with low-pressure steam, or steam of the tension of one atmosphere. An equivalent effect may be produced at the same expense of steam, by filling one-fourth of the cylinder with steam of the tension of four atmospheres, and loading the piston with four tons, which will be raised one foot. But the piston being raised one foot by steam of four atmospheres, and in the position represented in fig. 26, the supply of steam may be cut off, and the piston will continue to be elevated in the cylinder by the simple expansion of the steam below it, although with a diminishing force. When the piston has been raised another foot in the cylinder, or two feet from the bottom, the volume of the steam will be doubled, and its tension consequently reduced from four to $\frac{4}{2}$, or two atmospheres. At a height of three feet in the cylinder, the piston will have steam below it of the tension of $\frac{4}{3}$ or $1\frac{1}{3}$ atmosphere, and when the piston is elevated four feet, or reaches the top of the

Fig. 26.



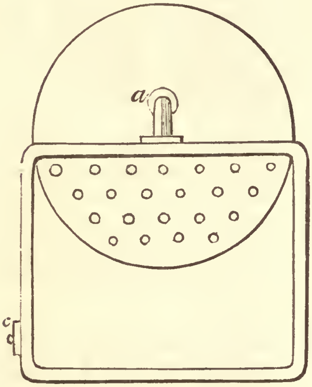
cylinder, the tension of the steam below it will still be $\frac{4}{4}$, or one atmosphere. The piston has, therefore, been raised to a height of three feet, with a force progressively diminishing from four atmospheres to one, or with an average force of two atmospheres, by means of a power acquired without any consumption of steam; but by the expansion merely of steam that had already produced its usual effect.[1]

Fig. 27.



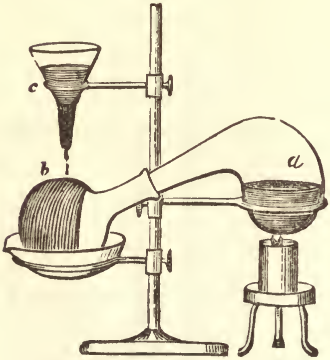
The boiler used to produce the steam is constructed of different forms. The cylinder boiler, of which a section is given in fig. 27, was found the most economical for the great steam-engines at the Cornish mines, and its use is extending in other quarters. It consists of two cylinders, one within the other, the smaller cylinder containing the fire, and the space between the two cylinders being occupied by the water. The outer cylinder may be six feet in diameter, and is often fifty or sixty feet in length. The heated air from the fire, after traversing the inner cylinder, is conducted under the boiler by the flues *o*, *o*, before it is conveyed to the chimney.

Fig. 28.



In the locomotive steam-engines, where the principal object is to generate steam in a small and compact apparatus with great rapidity, a different construction is adopted. Here the boiler consists of two parts, a square box with a double casing (of which a section or end view is given in figure 28), which contains the fire *f*, surrounded by a thin shell of water in the space *e e*, between the casings; and a cylinder *a*, through the lower part of which pass a number of copper tubes of small size, which communicate at one end with the fire-box, and at the other with the chimney, and form a passage for the heated air from the fire to the chimney. By means of these tubes, the object is accomplished of exposing to a source of heat the greatest possible quantity of surface in contact with the water. (See Dr. Lardner on the Steam-Engine: Cabinet Cyclopœdia.)

Fig. 29.



The subject of distillation is a natural sequel to vaporization; but it is unnecessary to enter into much detail. The principal point to be attended to is the most efficient mode of condensing the vapour. Figure 29 represents the ordinary arrangement in distilling a liquid from a retort *a*, and condensing the vapour in a glass flask *b*, which is kept cool by water dropping upon it from a funnel above, *c*. The condensing flask is covered by bibulous paper, so that the water falling upon it may be made to pass

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[1] For the mathematical theory of the steam-engine, see a Memoir on the Motive Power of Heat, by E. Clapeyron, Taylor's Scientific Memoirs, vol. i. p. 347; a Memoir on the Heat and Elasticity of Gases and Vapours, by C. Holtzmann, ibid. vol. iv. p. 169; Experiments on the Expansive Force of Steam, by Prof. G. Magnus, ibid. p. 218; and on the Force requisite for the Production of Vapours, by the same, ibid. p. 235.

equally over its surface, and it is supported in a basin likewise containing cold water.

But a much superior instrument to the condensing flask is the condensing tube of Professor Liebig (fig. 30). This is a plain glass tube, *t t*, about thirty inches in length, and one inch internal diameter, which is enclosed in a larger tube, *b*, of brass or tin-plate, about two feet long and two inches in diameter, the ends of which are closed by perforated corks, made fast by a mixture of white and red lead with a drying oil, a resinous cement being useless for such a junction. Or, the lower opening may be contracted by a collar of tin-plate, not much wider than the glass tube, and the two be united by a strong ring of sheet caoutchouc. A constant supply of cold condensing water from a vessel *a* is introduced into the space between the two tubes, being conveyed to the lower part of the instrument by the funnel and tube *f*, and flowing out from the upper part by the tube *j*. The condensed liquid drops quite cool from the lower extremity of the glass tube, where a vessel *c* is placed to receive it. The spiral copper tube or worm which is used for condensing in the common still is commonly made longer than is necessary, and, from its form, cannot be examined and cleared like a straight tube. Much vapour may be condensed by a small extent of surface, provided it is kept cold by an ample supply of condensing water.

Fig. 30.

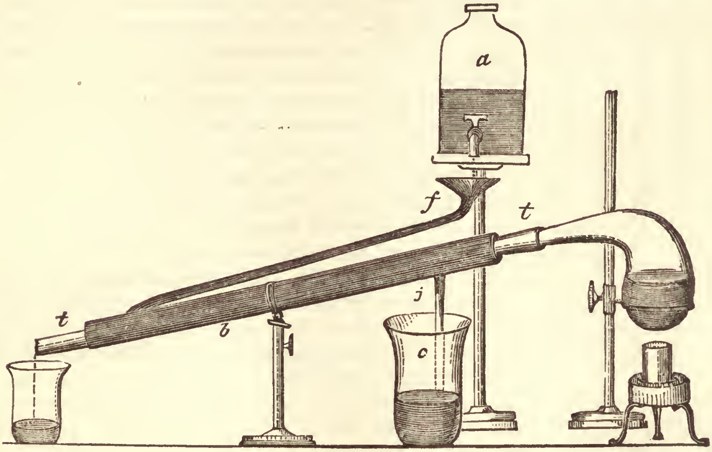


Fig. 31.

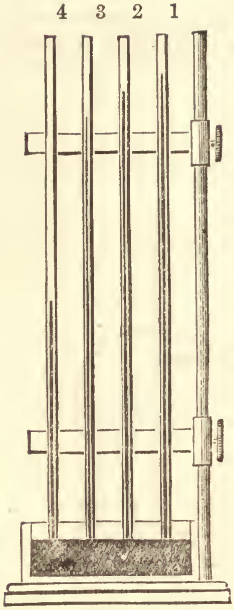
Both the outer and inner tube may be of glass in the condensing apparatus which has been described, and then the small tubes to bring and carry off the condensing water may be made to pass through openings in the corks, which they fit, as represented in figure 31.

EVAPORATION IN VACUO.

Water rises rapidly in vapour into a vacuous space, without the appearance of ebullition, at all temperatures, even at 32°, and greatly lower. Its elastic force increases as the temperature is elevated, till at 212° it is equal to that of the atmosphere, or capable of supporting a column of mercury thirty inches in height.

Various other solid and liquid substances emit vapour in similar circumstances; such as camphor, alcohol, ether, and oil of turpentine. Such bodies are said to be *volatile,* and other bodies, such as marble, the metals, &c. which do not emit a sensible vapour at the temperature of the air, are said to be *fixed.* All bodies which boil at low temperatures belong to the volatile class. An accurate estimate of the volatility of different bodies is obtained by determining the elastic force of the vapour which they emit in the vacuous space above the column of mercury in the barometer. If we pass up a bubble of air into the vacuum of the barometer, above the mercurial column, standing at the time at a height of 30 inches, the mercury is depressed, we may suppose, to the level of 29 inches, or by one inch. This would indicate that the air, by rising above the mercury, has been expanded into thirty times its former bulk, or that the elastic force of this rare air is equal to a column of one inch of mercury. The elastic force of vapour is estimated in the same manner. A few drops of the liquid operated upon are passed up into the vacuum above the mercurial column, which is depressed in proportion to the elastic force of the vapour. The depression produced by various liquids is very different, as illustrated in the annexed figure, representing four barometer tubes, in which the mercury is at its proper height in No. 1; is depressed by the vapour of water of the temperature 60° in No. 2; and by alcohol and ether at the same temperature in Nos. 3 and 4 respectively.

Fig. 32.



The depression of the mercurial column produced by water at every degree of temperature, between 32° and 212°, was first determined by Dr. Dalton, afterwards by M. Kaemtz, (Kaemtz, Meteorology, edited by C. Walker, p. 69), and again quite recently by M. Regnault, (Annales de Chimie, 3d sér. t. xi. p. 333; and t. xv. p. 139). The following selected observations prove that the elasticity increases at a very rapid rate with the temperature.

VAPOUR OF WATER IN VACUO (*Regnault*).

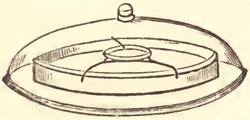
Temperature.		Tension in Millimeters and English inches of Mercury.	
Centig.	Fahr.	Millimeters.	English Inches.
—30°	—22°	0·365	0·0144
—25°	—13°	0·553	0·0218
—20°	—4°	0·841	0·0331
—15°	—5°	1·284	0·0506
—10°	14°	1·963	0·0818
—5°	23°	3·004	0·1233
0°	32°	4·600	0·1811
5°	41°	6·534	0·2573
10°	50°	9·165	0·3608
15°	59°	12·699	0·5000
20°	68°	17·391	0·6847
25°	77°	23·550	0·9272
30°	86°	31·548	1·2421
35°	95°	41·827	1·6468
60°	140°	148·791	5·8583
85°	185°	433·041	7·0488
100°	212°	760·000	29·9220

The vapours of other liquids increase in density and elastic force with the temperature, as well as the vapour of water; but each vapour appears to follow a rate of progression peculiar to itself.[1]

The assumption of latent heat by such vapours is evinced in some processes for producing cold. Water may be frozen by the evaporation of ether in the air-pump, and a cold produced of 55 degrees under the zero of Fahrenheit by the evaporation of that fluid. The ether vapour derives its store of latent heat from the remaining fluid and contiguous bodies, which being robbed of their heat, suffer a great refrigeration. To sustain the evaporation of this fluid, it is necessary to withdraw the vapour as it is produced by continual pumping. The volatile liquid, sulphuret of carbon, substituted for ether, produces even greater effects.

On the same principle is founded Leslie's elegant process for the freezing of water by its own evaporation, within the exhausted receiver of an air-pump, the evaporation being kept up by the absorbent power of sulphuric acid. (Supp. Encycloped. Britt., Art. Cold). A little water in a cup of porous stone-ware is supported over a shallow basin containing sulphuric acid (fig. 33). All that is necessary is to produce a good exhaustion at first: the processes of evaporation and absorption then go on spontaneously, in an uninterrupted manner. Various bodies, which have a powerful attraction for watery vapour, may be used as absorbents, such as parched oatmeal, the powder of mouldering whinstone, and even dry sole leather, by means of any one of which a small quantity of water may be frozen, during summer, in the exhausted receiver of an air-pump. No substance, however, is superior, in this respect, to concentrated sulphuric acid. When this liquid becomes too dilute to act powerfully as an absorbent, it may be rendered again fit for use, by boiling it and driving off the water. Ice might be procured in quantity, in a warm climate, by this process. The necessary vacuum would be most easily commanded, on the large scale, by allowing the receivers to communicate with a strong drum, filled with steam which could be condensed.

FIG. 33.



In the *Cryophorus* of Dr. Wollaston, water is also frozen by its own evaporation. This instrument consists of two glass bulbs, connected by a tube, and containing a portion of water, as represented in the figure. The air is first entirely expelled from the instrument by boiling the water, in both bulbs, at the same time, and allowing the steam to escape by a small opening at the extremity of the little projecting tube *e*. While the instrument is entirely filled with steam, the point of *e* is fused by the blow-pipe flame, and the opening hermetically closed. In experimenting with this instrument, the water is all poured into one bulb, and the other, or empty bulb, placed in a basin containing a mixture of ice and salt. The vapour in the cooled bulb is condensed, but its place is supplied by vapour from the water in the other bulb. A rapid evaporation takes place in the water bulb, and condensation in the empty bulb, till the water in the former bulb is cooled so low as to freeze. The instrument derives its name of the *cryophorus*, or frost-bearer, from this transference of the cold of the bulb in the freezing mixture to the bulb at a distance from it.

FIG. 34.

The question arises, do those bodies which evaporate at a moderate temperature continue to evaporate at all temperatures, however low. The opinion has prevailed,

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[1] For the tension of the vapour of mercury at different temperatures, see a memoir of M. Avogadro, Annales de Chimie, &c., t. xlix. p. 369. For other vapours, the article *Dampf*, in the Handwörterbuch der Chemie, &c. of Liebig, Poggendorff, and Wöhler; and the memoir by Mr. Faraday, On the Liquefaction and Solidification of Bodies generally existing as Gases, (Philos. Trans. 1845, p. 155).

that bodies which are decidedly vaporous at high temperatures, such as sulphuric acid and mercury, never cease to evolve vapour, however far their temperature may be depressed, although the quantity emitted becomes less and less, till it ceases to be appreciable by our senses. Even fixed bodies, such as metals, rocks, &c., have been supposed to allow an escape of their substance into air at the ordinary temperature; and hence the atmosphere has been supposed to contain traces of the vapours of all the bodies with which it is in contact. Certain researches of Mr. Faraday, published in the Philosophical Transactions for 1826, on the existence of a limit to vaporization, establish the opposite conclusion. Mercury was found to yield a small quantity of vapour during summer, at a temperature varying from 60° to 80°, but in winter no trace of vapour could be detected. Mr. Faraday has proved that several chemical agents, which may be volatized by a heat between 300° and 400°, did not undergo the slightest evaporation when kept in a confined space with water during four years.

Bodies, therefore, cease all at once to emit vapour, at some particular temperature. In mercury, this temperature lies between 40° and 60° Fahrenheit. But a progressive and endless diminution of vaporizing power is certainly more natural than an abrupt cessation. What puts a stop to vaporization? it may be asked. Liquids, we know, have a certain attraction for their own particles, evinced in their disposition to collect into drops. The particles of solids are attracted more powerfully, and cohere strongly together. Mr. Faraday is of opinion, that when the vaporizing power becomes weak, at low temperatures, it may be overcome and negatived completely by this cohesive attraction, and no escape of particles in the vaporous form be permitted.

This supposition is conformable with the views of corpuscular philosophy which were entertained by Laplace. According to that profound philosopher, the form of aggregation which a body affects depends upon the mutual relation of three forces: 1. The attraction of each particle for the other particles which surround it, which induces them to approach as near as possible to each other. 2. The attraction of each particle for the heat which surrounds the other particles in its neighbourhood. 3. The repulsion between the heat which surrounds each particle, and that which surrounds the neighbouring particles — a force which tends to disunite the particles of bodies. When the first of these forces prevails, the body is solid; if the quantity of heat augments, the second force becomes dominant, the particles then move among each other with facility, and the body is liquid. While this is the case, the particles are still retained by the attraction for the neighbouring heat, within the limits of the space which the body formerly occupied, except at the surface, where the heat separates them, that is to say, occasions evaporation, till the influence of some pressure prevents the separation from being effected. When the heat increases to such a degree that the reciprocal repulsive force prevails over the attraction of the particles for one another, they disperse in all directions, as long as they meet no obstacle, and the body assumes the gaseous form. Berzelius adds the reflection, that if, in that gaseous state into which Cagnard de la Tour reduced some volatile liquids, the pressure does not correspond with the result of calculation, that difference may depend on this: that, as the particles have not an opportunity to recede much, the two first forces continue always to act, and oppose the tension of the gas, which does not establish itself in all its power unless when the particles are so distant from each other as to be out of the sphere of the influence of these forces. (Traité de Chimie, par J. J. Berzelius, t. i. p. 85).

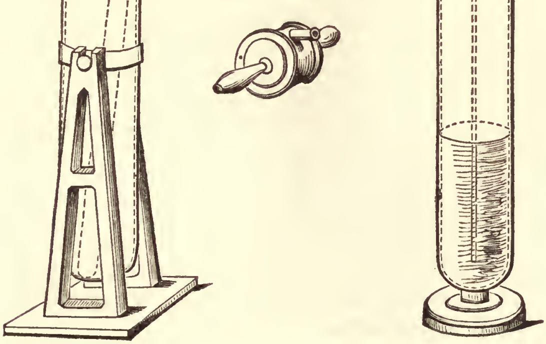
GASES.

Permanent gases, such as atmospheric air, unquestionably owe their elastic state to the possession of latent heat. But the theory of the similar constitution of gases and vapours, although supported by strong analogies, was not generally adopted by chemists, till it was experimentally confirmed by Faraday, who first liquefied several of the gases. (Philosophical Transactions, 1823, pp. 160, 189; and 1845, p. 155). His method was to generate the gas in one end of a strong glass tube, bent in the middle, as represented (fig. 35); and hermetically sealed. The gas accumulating in a confined space, comes to exert a prodigious pressure; an effect of which is, that a portion of the gas itself condenses into a liquid in the end of the tube most remote from the materials, which is kept cool with that view. Considerable danger is to be apprehended by the operator in conducting such experiments, from the bursting of the glass tubes, and the face ought always to be protected by a wire-gauze mask from the effects of an explosion. The names of the gases which were liquefied in this manner, are sulphurous acid, cyanogen, chlorine, ammoniacal gas, sulphuretted hydrogen, carbonic acid, muriatic acid, and nitrous oxide; which required a degree of pressure varying, in the different gases, from two atmospheres, in the first mentioned, to fifty atmospheres, in the last mentioned gas, at the temperature of 45°. The liquefaction of several of these gases has since been effected by the application of cold alone, without compression.

Fig. 35.

The principle of Faraday's condensing tube has been embodied in the machine of Thilorier for the liquefaction of carbonic acid gas. (Annales de Chimie, &c. 1835, lx. 427, 432). It consists (fig. 36) of two similar cylindrical vessels of wrought iron, made exceedingly strong, of the capacity of about three-fourths of a gallon, each of which is provided with a peculiarly constructed stopcock, being a spherical plug of lead on a spindle which can be screwed down, by turning the handle above, into a spherical cavity of brass-work, having at its base a tubular opening into the cylinder, which is thus closed. There is also a connecting tube of copper, the ends of which can be attached by screws to the discharging orifices of the stopcocks, so as to unite the two cylinders when necessary. The stopcock being

Fig. 36.



removed from one of the cylinders *a*, which is called the generator, a charge is introduced, consisting of two pounds of pulverulent bicarbonate of soda and three pounds of water at the temperature of 90°. After stirring these well together with a wooden rod, a quantity amounting to one pound three ounces of undiluted oil of vitriol is added, the latter being contained in a long cylindrical vessel of brass, sufficiently narrow to enter the generator, into which it is carefully let down by a hook without spilling. The stopcock being now applied to the mouth of the generator, and firmly screwed down upon it, with the intervention of a leaden washer, the generator is turned round upon its supporting pivots, so as completely to invert it; the brass measure within is thus canted over, and the acid which it contained mixed with the solution of soda. The carbonic acid of the salt, which amounts to half its weight, is thus disengaged, and accumulates with great elastic force in the vacant part of the generator. The charge of gas is then transferred to the other large cylinder, which is used as a receiver, by attaching it to the generator by the connecting tube, and after the lapse of five minutes, opening the stopcocks of both. It is advisable to have a woollen case or bag about the receiver, to hold fragments of ice for cooling it. The cylinders may again be separated, after shutting the stopcocks, and the same operations repeated. After two or three charges of gas are conveyed into the receiver, the pressure of the latter becomes sufficient to liquefy the gas; and after five or six charges the receiver may contain several pints of liquid carbonic acid. The receiver being finally detached is set aside, and the liquid it contains preserved for use.

When this highly volatile liquid is allowed to escape into air it evaporates so readily that one portion is instantly resolved into gas, and another portion is cooled so low by the heat thus abstracted as to freeze. From the stopcock of the receiver, a small tube, shown in the figure, descends to near the bottom and dips into the liquid; so that upon opening the former it is the liquid, and not gaseous carbonic acid, which escapes. A nozzle, being applied to the receiver, the stream of liquid is directed into a small cylindrical box of thin copper, with hollow wooden handles, which is soon filled with solid carbonic acid, in the form of a white substance like snow, or more closely resembling anhydrous phosphoric acid, from its opacity and entire want of crystallization.

Solid carbonic acid is a very bad conductor of heat, and may, therefore, be handled without injury, although its temperature is supposed to be so low as —100° C., or —148° Fahr.; and also preserved in the air for hours, if a considerable mass of it in a glass vessel be placed within another similar and larger glass vessel, with any non-conducting material between them. When applied to produce cold, in order to give it contact the solid carbonic acid is mixed with a little ether, with which it unites and forms a soft semifluid mass like half melted snow, capable of abstracting heat and evaporating rapidly, by means of which mercury can be frozen in large quantities, and an alcohol thermometer sunk in the open air so low as —135° (Thilorier). The apparatus of Thilorier forms thus an invaluable cold-producing machine.

Mr. Faraday has since produced a still lower degree of cold by placing a bath of Thilorier's mixture of solid carbonic acid and ether in the receiver of an air-pump, from which the air and gaseous carbonic acid were rapidly removed. The bath consisted of an earthenware dish of the capacity of four cubic inches or more, which was fitted into a similar dish somewhat larger, with three or four folds of dry flannel intervening; with the mixture in the inner dish such a bath lasted for twenty or thirty minutes, retaining solid carbonic acid the whole time. An alcohol thermometer placed in the bath, merely covered with paper, fell to —106°; and in the air-pump receiver, exhausted to within 1·2 inch mercury of a vacuum, the thermometer fell to —166°; or a cold of 60 degrees additional was produced by promoting the evaporation in this manner. At this low temperature the solid carbonic acid mixed with ether, was not more volatile than water at the temperature of 86°, or alcohol at ordinary temperatures.

By combining this extreme cooling power with the effect of mechanical pressure upon gases, several most interesting results were obtained. To produce the pressure, Mr. Faraday employed two condensing syringes, fixed to a table, the first having a piston of an inch in diameter, and the second a piston of only half an inch in diameter; and these were so associated by a connecting pipe, that the first pump forced the gas into and through the valves of the second, and then the second could be employed to throw forward this gas, already condensed to ten or twenty atmospheres, into its final recipient, the condensing tube, at a much higher pressure.

The condensing tubes were of green bottle-glass, being from $\frac{1}{6}$th to $\frac{1}{4}$th of an inch external diameter, and from $\frac{1}{42}$d to $\frac{1}{30}$th of an inch in thickness. They were of two kinds, about nine and eleven inches in length: one, in form of an inverted syphon (fig. 37), could have the bend cooled by immersion into a cold bath, and the other, horizontal (fig. 38), having a curve downward near one end to be cooled in the same manner. Into the longest leg of the syphon tube, and the straight part of the horizontal tube, minute pressure gauges were introduced when required. The caps, stopcocks, and connectors, were attached to the tubes by common cement,[1] and the screw joints made tight by leaden washers.

Fig. 37.

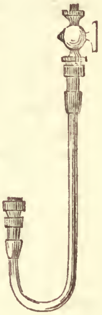


Fig. 38.

With the apparatus described, olefiant gas, which had not previously been liquefied, was condensed into a colourless transparent fluid, but did not become solid at the lowest temperature. The tension of its vapour was 4·6 atmospheres at —105°, and 26·9 atmospheres at 0° Fahr.; but Mr. Faraday is doubtful whether the condensed fluid can be considered as one uniform body. Hydriodic acid gas, which is easily liquefied, having a tension of 2·9 atmospheres only at 0° Fahr., was found to freeze at —60°, and to form a clear, colourless solid, resembling ice. Hydrobromic acid became a solid crystalline body at —124°. Fluosilicic acid gas liquefied under a pressure of about 9 atmospheres, at about 160° below zero, and was then clear, transparent, colourless, and very fluid, like hot ether; it did not freeze at any temperature to which it could be submitted; it has since been solidified by M. Natterer. The results obtained with fluoboric acid were similar. Phosphuretted hydrogen, subjected to high pressure, was condensed into a colourless liquid by the most intense degree of cold attainable, but was not solidified by any temperature applied.

Of gaseous bodies previously condensed, hydrochloric acid did not freeze at the lowest attainable temperature; the tension of its vapour was 1·8 atmospheres at —100°, 15·04 atmospheres at 0°, 26·20 atmospheres at 32°, and 30·67 atmospheres at 40°. Sulphurous acid became a crystalline, transparent, and colourless solid body at —105°; the pressure of the vapour of liquid sulphurous was 0·726 atmospheres at 0° Fahr., 1·53 atmospheres at 32°, 2 atmospheres at 46°·5, 3 atmospheres at 68°, 4 atmospheres at 85°, 5 atmospheres at 98°, and 6 atmospheres at 110°.

Sulphuretted hydrogen solidified at —122°, forming a white crystalline translucent substance, more like nitrate of ammonia solidified from the melted state, or camphor, than ice. The pressure of the vapour from the solid is not more, probably, than 0·8 of an atmosphere, so that the liquid allowed to evaporate in the air would not solidify as carbonic acid does. The tension of sulphuretted hydrogen vapour was 1·02 atmosphere at —100°, 2 atmospheres at —58°, 6·1 atmospheres at 0°, 9·94 atmospheres at 30°, and 14·6 atmospheres at 52°, which form a progression considerably different from that of water or carbonic acid.

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[1] Five parts of resin, one part of yellow bees'-wax, and one part of red ochre, by weight, melted together.

Mr. Faraday observed, that when carbonic acid is melted and resolidified by a bath of low temperature, it appears as a clear transparent crystalline colourless body, like ice. It melts at —70° or —72°, and the solid carbonic acid is heavier than the liquid bathing it. The solid or liquid carbonic acid, at this temperature, has a pressure of 5·33 atmospheres. Hence the facility with which liquid carbonic acid, when allowed to escape into air, exerting only a pressure of one atmosphere, freezes a part of itself by the evaporation of another part. The following are the pressures of the vapours of carbonic acid which Mr. Faraday has obtained:—

CARBONIC ACID VAPOUR.

Temp. Fahr.	Tension in Atmospheres.	Temp. Fahr.	Tension in Atmospheres.
—111°	1·14	—15°	17·80
—107	1·36	— 4	21·48
— 95	2·28	0	22·84
— 83	3·60	5	24·75
— 75	4·60	10	26·82
— 56	6·97	15	29·09
— 34	12·50	23	33·15
— 23	15·45	32	38·50

Nitrous oxide was obtained solid, as a beautiful clear crystalline colourless body, by a temperature estimated at about —150°, when the pressure of its vapour was less than one atmosphere. Mr. Faraday believes that liquid nitrous oxide may be used instead of carbonic acid, to produce degrees of cold far below those which the latter body can supply. This idea was verified by M. Natterer, who has liquefied nitrous oxide, and several other gases, by mechanical compression. He found that liquid nitrous oxide may be mixed with sulphuret of carbon in all proportions, and on placing a mixture of these two liquids under the receiver of an air-pump, he saw an alcohol thermometer fall to —140° C., or —220° Fahr.; at this extremely low temperature neither chlorine nor the sulphuret of carbon lost its fluidity. He also succeeded in freezing liquid fluosilicic acid by the same means (Poggendorff's Annalen, t. xii. p. 132: and Liebig's Annalen, t. liv. p. 254). The tension of its vapour was observed by Faraday to be, atmosphere at —125°, 19·34 atmospheres at 0°, and 33·4 atmospheres at 35°.

Liquid cyanogen, when cooled, becomes a transparent crystalline solid, as Bussy and Bunsen had previously observed,[1] which liquefies at —30°. The tension of its vapour was 1·25 atmospheres at 0°, 2·37 atmospheres at 32°, and 6·9 atmospheres at 63°.

Ammonia formed a white, translucent, crystalline solid, melting at —103°. The density of the liquid was 0·731 at 60°; its tension 2·48 atmospheres at 0°, 4·44 atmospheres at 32°, and 6.9 atmospheres at 60°.

Arsenietted hydrogen, which was liquefied by Dumas and Soubeiran, did not solidify at —166°. The tension of its vapour was 0·94 atmospheres at —75°, 5·21 atmospheres at 0°, 8·95 atmospheres at 32°, and 13·19 atmospheres at 60°.

The following gases showed no signs of liquefaction when cooled by the carbonic acid bath in vacuo, at the pressure expressed:—

	Atmospheres.
Hydrogen at	27
Oxygen	58·5
Nitrogen	50
Nitric oxide	50
Carbonic oxide	40
Coal gas	32

Several gases were submitted by M. G. Aimé to still higher pressures, rising for nitrogen and hydrogen gases to 220 atmospheres, by immersion in the depths of the

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[1] For Bunsen's results on the liquefaction of several of the gases, see Bibliothèque Universelle, 1839, t. xxxii. p. 185.

sea, where the results under pressure could not be observed (Annales de Chimie, &c. 1843, 3d ser. t. viii. p. 275). Most of them were diminished in bulk in a ratio greatly exceeding the pressure; but this has been shown to be often the case whilst the substance retains the gaseous form. No sufficient evidence of the liquefaction of any of the gases just enumerated has yet been produced. The same may be said of light carburetted hydrogen. At the lowest temperatures attainable, alcohol, ether, sulphuret of carbon, chloride of phosphorus, and chlorine, also retained the liquid form.

Sir H. Davy threw out the idea that the prodigious elastic force of the liquid gases might be used as a moving power. But supposing the application practicable, it may be doubted, from what we know of the constancy of the united sum of the latent and sensible heat of high pressure steam, whether any saving of heat would be effected by such an application of the vapours of these fluids.

All gases whatever are absorbed and condensed by water in a greater or less degree, in which case they certainly assume the liquid form. The quantity condensed is widely different in the different gases; and in the same gas the quantity condensed depends upon the pressure to which the gas is subject, and the temperature of the absorbing water. Dr. Henry proved that with carbonic acid gas the *volume* absorbed by water is the same, whatever be the pressure to which the gas is subject. Hence, we double the weight or quantity of gas absorbed, by subjecting it, in contact with water, to the pressure of two atmospheres; and this practice is adopted in impregnating water with carbonic acid, to make soda-water. The colder the water, the greater also the quantity of gas absorbed.

In the physical theory of gases, they are assumed to be expansible to an indefinite extent, in the proportion that pressure upon them is diminished, and to be contractible under increased pressure exactly in proportion to the compressing force — the well-known law of Mariotte. The bulk of atmospheric air has been found rigidly to correspond with this law, when it was expanded to 300 volumes, and also when compressed into 1-25th of its primary volume. But there is reason to doubt whether the law holds with absolute accuracy, in the case of a gas either in a state of extreme rarefaction, or of the greatest density. Thus atmospheric air does not appear to be indefinitely expansible, as the law of Mariotte would require; for there is certainly a limit to the earth's gaseous atmosphere, and it does not expand into all space. Dr. Wollaston supposed that the material particles of air are not indefinitely minute, but have a certain magnitude and weight. These particles are under the influence of a powerful mutual repulsion, as is always the case in gaseous bodies, and, therefore, tend to separate from each other; but as this repulsive force diminishes as the distance of the particles from each other increases, Dr. Wollaston imagined that the weight of the individual particles might come at last to balance it, and thus prevent their further divergence. On this view, which is probable on other grounds, the expansion of a gas, caused by the removal of pressure, will cease at a particular point of rarefaction, and the gas not expanding farther, will come to have an upper surface, like a liquid. The earth's atmosphere has probably an exact limit, and true surface.

The deviation from the law of Mariotte, in gases under a greater pressure than that of the atmosphere, has been distinctly observed in the more liquefiable gases. Thus, Professor Oersted, of Copenhagen, found that sulphurous acid gas diminishes, under increased pressure, more rapidly than common air. The volumes of atmospheric air and of the gas were equal at the following pressures:—

Pressure upon air in atmospheres.	Pressure upon sulphurous gas in atmospheres.
1	1
1.175	1.173
2.821	2.782
3.319	3.189

It will be observed that less pressure always suffices to reduce the sulphurous acid gas to the same bulk than is required by air. If the pressure upon the air and gas were made equal, then the gas would be compressed into less bulk than the air, and deviate from the law of Mariotte. Despretz observed an equally conspicuous deviation from this law under increasing pressures, in several other gases, particularly sulphuretted hydrogen, cyanogen, and ammonia, which are all easily liquefied. There is no reason, however, to suppose that any partial liquefaction of the gases occurs under the pressure applied to them in such experiments. They remain entirely gaseous, and their superior compressibility must be referred to a law of their constitution. It is the phenomenon beginning to show itself in a gas under moderate pressure, which was observed in all its excess by Cagnard de la Tour, in the vapours confined by him under great pressure (page 68).

Those gases which exhibit this deviation must occupy less bulk than they ought to do under the pressure of the atmosphere itself; which may be the reason why the liquefiable gases are generally found by experiment specifically heavier than they ought by theory to be.

M. Regnault accordingly finds, that at the temperature of 32°, and under more feeble pressures than that of the atmosphere, carbonic acid deviates from the law of Mariotte in a marked manner; while it appears to follow that law when heated to 212° under more feeble pressures than that of the atmosphere.

The density of carbonic acid at 33° (air = 1000) was :—

Under the pressure of 760 millimeters (30 inches)	1529.10
374.13	1523.66
224.17	1521.45

The density of the gas at 212° (that of air at the same temperature being 1000) was :—

Under the pressure of 760 millimeters (30 inches)	1524.18
338.39	1524.10

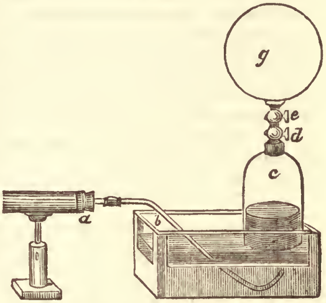
The theoretical density of carbonic acid, calculated in a manner which shall be afterwards explained, and taking for the atomic weight of carbon the number 6, is 1520.24; to which the numbers for the density of the gas under greatly reduced pressures appear to be converging. M. Regnault verified at the same time the exactness of the law of Mariotte for atmospheric air. (Annales de Ch., xiv. 227, and 234).

Such are the most remarkable features which gases exhibit in relation to pressure and temperature. These properties are independent of the specific weights of the gases, which are very different in the various members of the class, and they are but little connected with the nature of the particular substance or material which exists in the gaseous form. But when gases differing in composition are presented to each other, a new property of the gaseous state is developed, namely, the forcible disposition of dissimilar gases to intermix, or to diffuse themselves through each other. This is a property which interferes in a great variety of phenomena, and is no less characteristic of the gaseous state than any we have considered. It appears in the spontaneous diffusion of gases through each other, and in the diffusion of vapours into gases, or the ascent of vapours from volatile bodies into air and other gases, of which the spontaneous evaporation of water into the air is an instance. Related closely to this subject, and preliminary to its consideration, is the passage of different gases into a vacuum, through a small aperture, which takes place with different degrees of facility; with their rates of transmission by capillary tubes. The whole may be briefly treated under the heads of, (1) Effusion of gases (their pouring out), by which I express their passage into a vacuum by a small aperture in a thin plate; (2) Transpiration of gases, or their passage through tubes of fine bore of greater or less length; (3) The diffusion of gases; and (4) Evaporation in air.

EFFUSION OF GASES.

The specific weights, or weights of an equal measure, of the different gases vary exceedingly. The numbers representing these weights are always referred to the weight of a gas, generally air, as 1 or 1000, instead of water, which is the standard comparison for liquids and solids. The operation of taking the specific gravity of a gas is simple in principle, but the accurate execution of it is attended with great practical difficulties. A light glass globe *g* (fig. 39) from 50 to 100 cubic inches in capacity, is weighed full of air, then exhausted by an air-pump and weighed empty, the loss being taken as the weight of its volume of air. It is then, in its exhausted state, united with a bell-jar *c*, containing the gas to be weighed and standing over a mercurial trough, by a union screw between the stopcocks *d* and *e* of the two vessels; and filled with the gas, which rushes from the jar to the vacuous globe on opening both stopcocks. A supply of gas is conveyed to the jar by the bent tube *b*, after being deprived of moisture by passing through a drying tube *a*, containing fragments of chloride of calcium. The globe is again weighed when full of gas of the atmospheric pressure and temperature, and the weight of a volume of the gas obtained by deducting the weight of the vacuous globe. The specific gravity is then calculated by the proportion, as the weight of air first found, to the weight of gas, so 1.000 (density of air), to a number which expresses the density of the gas required. MM. Dumas and Boussingault, in their late careful observations of the density of oxygen, nitrogen, and hydrogen, employed a capacious glass globe, of which the cubic contents were first ascertained by measuring in an accurate manner the volume of water required to fill it (Annales de Chimie, 3d sér. viii. 201). In the refined experiments of M. Regnault, lately published, a light glass balloon of about ten litres or 616 cubic inches in capacity, was employed as the weighing globe. It was counterpoised, when weighed, by a similar globe formed of the same glass; by which arrangement numerous and somewhat uncertain corrections for variations in the density, temperature, and hygrometric state of the air, during the continuance of an experiment, the film of moisture which adheres to glass, and the displacement of air by the solid materials of the balloon, were entirely avoided. (Ibid., 1845, 3d sér. t. iv. 211).

Fig. 39.



The following tables exhibit the specific gravity of those gases to which reference will most frequently be made, air being taken as the standard of comparison in the first table, and oxygen in the second. To each specific gravity is added, in a second column, the square root of the number, and in a third column 1 divided by the square root, or the reciprocal of the square root.

TABLE I. DENSITY OF GASES, AIR = 1.

	DENSITY.	SQUARE ROOT OF DENSITY.	$\frac{1}{\text{SQUARE ROOT.}}$	AUTHORITY.
Nitrogen	0·97137	0·9856	1·0147	Regnault.
Oxygen	1·10563	1·0515	0·9510	"
Hydrogen	0·06926	0·2632	3·7994	"
Carbonic acid	1·52901	1·2365	0·8087	"
Carbonic oxide	0·9712	1·9855	1·0147	Calculated.
Light carburetted hydrogen	0·5549	0·7449	1·3424	"
Olefiant gas	0·9712	0·9855	1·0147	"
Nitrous oxide	1·5261	1·2353	0·8095	"
Nitric oxide	1·0405	1·0205	0·9799	"
Sulphuretted hydrogen	1·1793	1·0860	0·9208	"
Chlorine	2·4573	1·5676	0·6379	"

TABLE II. DENSITY OF GASES, OXYGEN = 1.

GASES.	DENSITY.	SQUARE ROOT OF DENSITY.	$\frac{1}{\text{SQUARE ROOT.}}$	AUTHORITY.
Air	0·9038	0·9507	1·0518	Regnault.
Nitrogen	0·8785	0·9373	1·0669	"
Hydrogen	0·6626	0·2502	3·9968	"
Carbonic acid	1·3830	1·1760	0·8503	"
Carbonic oxide	0·8750	0·9354	1·0691	Calculated.
Light carburetted hydrogen CH^2	0·5000	0·7071	1.4142	"
Olefiant gas	0·8750	0·9354	1·0691	"
Nitrous oxide	1·3750	1·1705	0·8545	"
Nitric oxide	0·9375	0·9682	1·0328	"
Sulphuretted hydrogen	1·0625	1·0308	8·9701	"
Chlorine	2·2129	1·4876	0·6722	"

A jar on the plate of an air-pump is kept vacuous by continued exhaustion, and a measured quantity of air, or any other gas, allowed to find its way into the vacuous jar through a minute aperture in a thin metallic plate, such as platinum foil, made by a fine steel point, and not more than 1-300dth of an inch in diameter. With an imperfect exhaustion, it is found that the velocity with which the gas flows into the jar rapidly increases till the aspiration power or degree of exhaustion amounts to about one-third of an atmosphere. Higher degrees of exhaustion do not produce a corresponding increase of velocity, and the difference of an inch of the mercurial column of the gauge barometer scarcely affects the rate at which the gas enters, when the vacuum is nearly complete, and the pressure to which the gas is subject approaches that of a whole atmosphere. By a perforated plate such as described, 60 cubic inches of dry air entered the vacuous, or nearly vacuous air-pump receiver, in about 1000 seconds, and in successive experiments the time of passage did not vary more than one or two seconds.

The time of passage into a vacuum of a constant volume varied in the different gases, the lightest passing in the shortest time. The time corresponded very closely for each gas with the square root of its density. Thus the square root of the density of oxygen being 1·0515, and that of air 1, (Table I.), the time of passage of the constant volume of oxygen was observed to be 1·0519, 1·0519, 1·0506, 1·0502, in experiments made on different occasions, the time of passage of the same volume of air being 1. Compared with the time of the passage of a constant volume of oxygen taken as 1, the time of hydrogen was 0·2631, instead of 0·25 (Table II.); the time of nitrogen was 0·9365 and 0·9345, instead of 0·9373; the time of carbonic oxide, of which the theoretical density is the same as the last gas, was 0·9345, instead of 0.9354; of carburetted hydrogen 0·7023, instead of 0·7071; of carbonic acid 1·1675, instead of 1·1705. The time of nitrous oxide was always the same, as nearly as could be observed, as that of carbonic acid; while these two gases have the same specific gravity. For gases which do not differ greatly from air in specific gravity, the times correspond so closely with the law, that the densities of these gases, it appears, might be deduced as accurately from an effusion experiment as by actually weighing them. The sensible deviation from the law in the times of both the very light and very heavy gases can be shown to be occasioned by the tubularity of the aperture arising from the unavoidable thickness of the metallic plate.

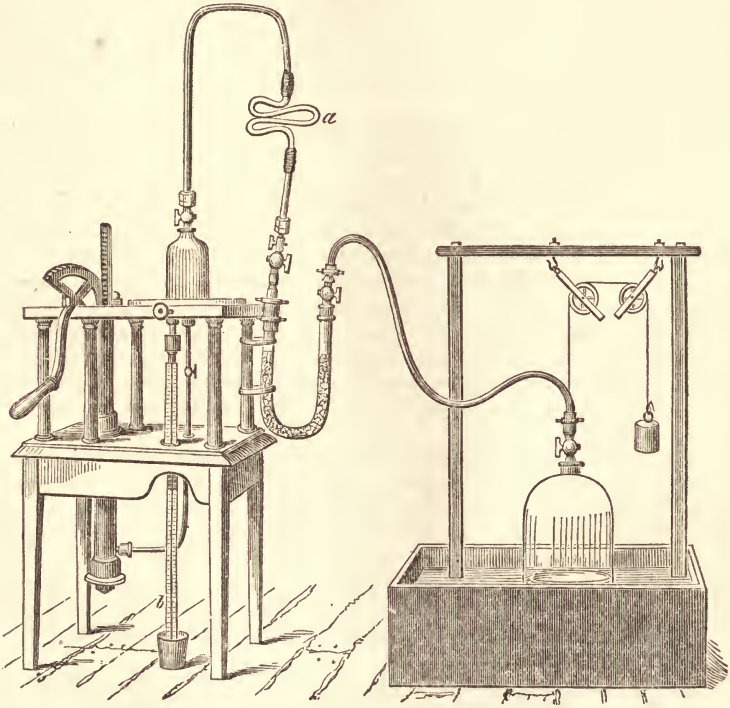
The times of passage into a vacuum of equal volumes of different gases varying, then, as the square root of their densities, the velocities of passage will consequently be in the inverse proportion, or as 1 divided by the square root of the gas. This is the physical law of the passage of fluids generally under pressure, which has been long established for liquids of different densities by observation, but had not previously received an experimental verification in the case of gases.

Mixtures of nitrogen and oxygen in different proportions were found to have the mean rate of their constituent gases. This is also true of mixtures of carbonic acid, nitrous oxide, and carbonic oxide, with each other or with the preceding gases. But hydrogen and carburetted hydrogen lose more or less of their peculiar rate, and pass slower, when mixed with other gases. Thus the time of passage of a mixture of equal volumes of oxygen and hydrogen is 0·7255; instead of 0·6315, the mean of the times, 1 and 0·2631, of those gases individually. Supposing the rate of the oxygen in the mixture to remain unchanged, and that the alteration takes place on the hydrogen exclusively, then the time of passage of the hydrogen has increased from 0·2631 to 0·4510, or been nearly doubled. But it is in mixtures where the proportion of hydrogen is large compared with that of the other gas, that the departure from the mean velocity is most conspicuous. Thus the addition of half a per cent. of air or oxygen has an effect in retarding the passage of hydrogen at least three times greater than what it should produce from its greater density by calculation. The time of the effusion of hydrogen thus becomes a delicate test of the purity of that gas. This want of mechanical equivalency in hydrogen mixtures is exceedingly remarkable, being a marked departure from the usual uniformity of gaseous properties.

TRANSPIRATION OF GASES.

The arrangement exhibited (fig. 40), was adopted in examining the rates of passage of different gases into a vacuum through a capillary tube. The gas is taken from a counterpoised bell-jar, standing over the water of a pneumatic trough, and passes first by a flexible tube to a U-shaped drying tube filled with fragments of chloride of calcium, in order to be deprived of aqueous vapour before entering the capillary

Fig. 40.



glass tube *a*. The last is connected by means of a tube of block tin with a receiver on the plate of an air-pump, provided with a gauge barometer *b*, as represented. Gas is allowed to enter the exhausted receiver by the capillary tube, and the time observed which the gauge barometer requires to fall a certain number of inches from the admission of a constant volume.

It is found that for a tube of any given diameter, the times of passage of different gases approximate the more closely to their respective times of effusion, the more the tube is shortened and made to approximate to an aperture in a thin plate. While, as the tube is elongated, a deviation from those rates is observed, which is rapid with the first additions in length, but becomes gradually less; and, finally, with a certain length of tube, the gases attain rates of which the relation remains constant, or nearly so, for any farther increase of length. The same relation in velocity between the different gases is then found to extend also through a considerable range of pressure, as from one to one-tenth of an atmosphere.

The ultimate rates of transpiration differ considerably from the rates of effusion of the same gases, and have no uniform relation to their density. Of all the gases tried, oxygen passes with least velocity through a capillary tube. The time of passage into a vacuum, under the atmospheric pressure, of a volume of oxygen being 1, that of air was 0.9010, of nitrogen 0.8704, and carbonic oxide 0.8671. The transpiration times of these gases approach so closely to their specific gravities, as will be seen by Table II., as to lead to the inference that the transpiration times are directly as the density for these gases. Nitric oxide appears to coincide in transpiration time with nitrogen, although denser, the specific gravity of the former being the mean between the densities of the nitrogen and oxygen. The transpiration time of carbonic acid approached very closely to 0.75, or three-fourths of that of oxygen. Nitric oxide, which has the same specific gravity as carbonic acid, coincides perfectly with that gas also in time of transpiration. The densities of these two gases are to that of oxygen as 22 to 16, but their times of transpiration are to the time of transpiration of oxygen, as 12 to 16.

The transpiration time of hydrogen, by several capillary tubes, varied but very little from 0.44, the time of oxygen being 1. The number for hydrogen therefore approaches 0.4375, which is 7-16ths of the oxygen time. The time of light carburetted hydrogen was also remarkably constant at 0.550 to 0.555; which approach, although not very closely, to 0.5625, or 9-16ths of the oxygen time. Olefiant gas has probably sensibly the same specific gravity as nitrogen and carbonic oxide, but it is much more transpirable than these gases; the transpiration time of olefiant gas being found so low as 0.512. This result is not inconsistent with the true number for olefiant gas, being 0.5, or one-half the time of oxygen; for the gas operated upon was found always to contain either a trace of a heavy hydrocarbon, or a few per cent. of carbonic oxide, both of which increase the time of transpiration. Hydrogen with five per cent. of air was less rapidly transpired than olefiant gas, the time of that mixture being 0.5237.

The transpiration time of mixtures of the following gases was exactly the mean of the times of the mixed gases, namely, oxygen, nitrogen, hydrogen, carbonic oxide, nitrous oxide, and carbonic acid; but the transpiration time of hydrogen and carburetted hydrogen, particularly the former, is greatly increased when these gases are in a state of mixture with each other, or with gases of the former class. Thus the transpiration time of a mixture of equal volumes of oxygen and hydrogen was 0.9008, instead of 0.72, the mean time of the two gases. The transpiration time of hydrogen in such a mixture is as high as 0.8016; or, its transpiration is then less rapid than that of pure carbonic acid.

The effusion of a given measure of air into a vacuum takes place always in the same time, whatever may be its density, from one-fourth of an atmosphere up to two atmospheres. But the transpiration of air of different densities was observed to take place in times which are inversely as the densities; or, the denser air is, the more rapidly is a given volume of it transpired. Hence the transpiration of air and all gases is greatly affected by variations of the barometer; the higher the barometer the more quickly are the gases transpired. The difference in this respect separates completely the phenomena of effusion and transpiration. Nor can the phenomena of transpiration be an effect of friction, for the greater the density of air, the more should its passage be resisted by friction. The transpirability of a gas appears to be a constitutional property, like its density, or its combining volume; and the investigation is of peculiar interest from supplying a new class of constants for the gases, namely, their coefficients of transpiration. The rates of transpiration of different gases were further observed to be the same through a fine capillary tube of copper of eleven feet in length, and a mass of dry stucco, as through capillary tubes of glass.

DIFFUSION OF GASES.

When a light and heavy gas are once mixed together, they do not exhibit any tendency to separate again, on standing at rest; differing in this respect from mixed liquids, many of which speedily separate, and arrange themselves according to their densities, the lightest uppermost, and the heaviest undermost — as in the familiar example of oil and water, unless they have combined together. This peculiar property of gases has repeatedly been made the subject of careful experiment. Common air, for instance, is essentially a mixture of two gases, differing in weight in the proportion of 971 to 1105; but the air in a tall close tube of glass several feet in length, kept upright in a still place, has been found sensibly the same in composition at the top and bottom of the tube, after a lapse of months. Hence, there is no reason to imagine that the upper strata of the air differ in composition from the lower; or that a light gas, such as hydrogen, escaping into the atmosphere, will rise, and ultimately possess the higher regions; — suppositions which have been the groundwork of meteorological theories at different times.

The earliest observations we possess on this subject are those of Dr. Priestley, to whom pneumatic chemistry stands so much indebted. Having repeated occasion to transmit a gas through stoneware tubes surrounded by burning fuel, he perceived that the tubes were porous, and that the gas escaped outwards into the fire; while at the same time the gases of the fire penetrated into the tube, although the gas within the tube was in a compressed state.

Dr. Dalton, however, first perceived the important bearings of this property of aërial bodies, and made it the subject of experimental inquiry. He discovered that any two gases, allowed to communicate with each other, exhibit a positive tendency to mix or to penetrate through each other, even in opposition to the influence of their weight. Thus, a vessel *h*, containing a light gas (hydrogen), being placed above a vessel *c*, containing a heavy gas (carbonic acid), and the two gases allowed to communicate by a narrow tube, as represented (fig. 41), an interchange speedily took place of a portion of their contents, which it might be supposed that their relative position would have prevented. Contrary to the solicitation of gravity, the heavy gas continued spontaneously to ascend, and the light gas to descend, till in a few hours they became perfectly mixed, and the proportion of the two gases was the same in the upper and lower vessels. This disposition of different gases to intermix, appeared to Dr. Dalton so decided and strong, as to justify the inference that different gases afforded no resistance to each other; but that one gas spreads or expands into the space occupied by another gas, as it would rush into a vacuum. At least, that the resistance which the particles of one gas offer to those of another is of a very imperfect kind, to be compared to the resistance which stones in the channel of a stream oppose to the flow of running water. Such is Dalton's theory of the miscibility of the gases. (Manchester Memoirs, Vol. V.)

Fig. 41.

In entering upon this inquiry, I found, first, that gases diffuse into the atmosphere, and into each other, with different degrees of ease and rapidity. This was observed by allowing each gas to diffuse from a bottle into the air through a narrow tube, taking care, when the gas was lighter than air, that it was allowed to escape from the lower part of the vessel, and when heavier from the upper part, so that it had, on no occasion, any disposition to flow out, but was constrained to diffuse in opposition to the effect of gravity. The result was, that the same volume of different gases escapes in times which are exceedingly unequal, but have a relation to the specific gravity of the gas. The light gases diffuse or escape most rapidly: thus, hydrogen escapes five times quicker than carbonic acid, which is twenty-two times heavier than that gas. Secondly, in an intimate mixture of two gases, the most diffusive gas separates from the other, and leaves the receiver in the greatest proportion. Hence, by availing ourselves of the tendencies of mixed gases to diffuse with different degrees of rapidity, a sort of mechanical separation of gases may be effected. The mixture must be allowed to diffuse for a certain time into a confined gaseous or vaporous atmosphere, of such a kind as may afterwards be condensed or absorbed with facility. (Quarterly Journal of Science, New Series, Vol. V.)

But the nature of the process of diffusion is best illustrated when the gases communicate with each other through minute pores or apertures of insensible magnitude.

A singular observation belonging to this subject was made by Professor Dobereiner, of Jena, on the escape of hydrogen gas by a fissure or crack in glass receivers. Having occasion to collect large quantities of that light gas, he had accidentally made use of a jar which had a slight fissure in it. He was surprised to find that the water of the pneumatic trough rose into this jar one and a half inches in twelve hours; and that after twenty-four hours the height of the water was two inches two-thirds above the level of that in the trough. During the experiment, neither the height of the barometer nor the temperature of the place had sensibly altered. (Annales de Chimie et de Physique, 1825.) He ascribed the phenomenon to capillary action, and supposed that hydrogen only is attracted by the fissures, and escapes through them on account of the extreme smallness of its atoms. It is unnecessary to examine this explanation, as Dobereiner did not observe the whole phenomenon. On repeating the experiment, and varying the circumstances, it appeared to me that hydrogen never escapes outwards by the fissure without a certain portion of air penetrating at the same time inwards, amounting to between one-fourth and one-fifth of the volume of the hydrogen which leaves the receiver. It was found by an instrument which admits of much greater precision than the fissured jar, that when hydrogen gas communicates with air through such a chink, the air and hydrogen exhibit a powerful disposition to exchange places with each other; a particle of air, however, does not exchange with a particle of hydrogen of the same magnitude, but of 3.83 times its magnitude. We may adopt the word *diffusion-volume*, to express this diversity of disposition in gases to interchange particles, and say that the diffusion-volume of air being 1, that of hydrogen gas is 3.83. Now every gas has a diffusion-volume peculiar to itself, and depending upon its specific gravity. Of those gases which are lighter than air, the diffusion-volume is greater than 1, and of those which are heavier, the diffusion-volume is less than 1. The diffusion volumes are, indeed, inversely as the square root of the densities of the gases. Hence the times of the effusion and diffusion of gases follow the same law.*

Exact results are obtained by means of a simple instrument, which may be called a diffusion tube, and which is constructed as follows. A glass tube, open at both ends, is selected, half an inch in diameter, and from six to fourteen inches in length. A cylinder of wood, somewhat less in diameter, is introduced into the tube, so as to occupy the whole of it, with the exception of about one-fifth of an inch at one extremity, which space is filled with a paste of Paris plaster, of the usual consistence for casts. In the course of a few minutes the plaster sets, and on withdrawing the wooden cylinder the tube forms a receiver, closed by an immoveable plate of stucco. In the wet state, the stucco is air-tight; it is therefore dried, either by exposure to the air for a day, or by placing it in a temperature of 200° for a few hours; and is thereafter found to be permeable by gases, even in the most humid atmosphere, if

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* [*See Supplement*, p. 751.]

not positively wetted. When such a diffusion-tube, six inches in length, is filled with hydrogen over mercury, the diffusion, or exchange of air for hydrogen, instantly commences through the minute pores of the stucco, and proceeds with so much force and velocity, that within three minutes the mercury attains a height in the receiver of more than two inches above its level in the trough; within twenty minutes, the whole of the hydrogen has escaped. In conducting such experiments over water, it is necessary to avoid wetting the stucco. With this view, before filling the diffusion-tube with hydrogen, the air is withdrawn by placing the tube upon the short limb of an empty syphon (see figure 42), which does not reach, but comes within half an inch of the stucco, and then sinking the instrument in the water trough, so that the air escapes by the syphon, with the exception of a small quantity, which is noted. The diffusion tube is then filled up, either entirely or to a certain extent, with the gas to be diffused.

Fig. 43.

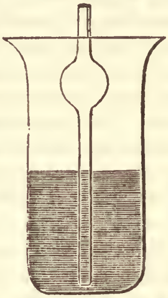
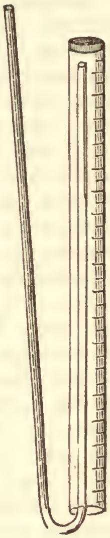


Fig. 42.



The ascent of the water in the tube, when hydrogen is diffused, forms a striking experiment. But in experiments made with the purpose of determining the proportion between the gas diffused and the air which replaces it, it is necessary to guard against any inequality of pressure, by placing the diffusion tube in a jar of water as in figure 43, and filling the jar with water in proportion as it rises in the tube.

In this instrument we may substitute many other porous substances for the stucco; but few of them answer so well. Dry and sound cork is very suitable, but permits the diffusion to go on very slowly, not being sufficiently porous; so do thin slips of many granular foliated minerals, such as flexible magnesian limestone. Charcoal, woods, unglazed earthenware, dry bladder, may all be used for the same purpose.

It can be shown, on the principles of pneumatics, that gases should rush into a vacuum with velocities corresponding to the numbers which have been found to express their diffusion volumes; that is, with velocities inversely proportional to the square root of the densities of the gases. The law of the diffusion of gasses has on this account been viewed by my friend, Mr. T. S. Thomson, of Clitheroe, as a confirmation of Dr. Dalton's theory, that gases are inelastic towards each other (L. Ed. and D., Phil. Mag. 3d series, iv. 321). It must be admitted that the ultimate result in diffusion is in strict accordance with Dalton's law, but there are certain circumstances which make me hesitate in adopting it as a true representation of the phenomenon, although it affords a covenient mode of expressing it. 1. It is supposed, on that law, that when a cubic foot of hydrogen gas is allowed to communicate with a cubic foot of air, the hydrogen *expands* into the space occupied by the air, as it would do into a vacuum, and becomes two cubic feet of hydrogen of half density. The air, on the other hand, expands in the same manner into the space occupied by the hydrogen, so as to become two cubic feet of air of half density. Now if the gases actually expanded through each other in this manner, cold should be produced, and the temperature of the mixed gases should fall 40 or 45 degrees. But not the slightest change of temperature occurs in diffusion, however rapidly the process is conducted. 2. Although the ultimate result of diffusion is always in conformity with Dalton's law, yet the diffusive process takes place in different gases with very different degrees of rapidity. Thus, the external air penetrates into a diffusion tube with velocities denoted by the following numbers, 1277, 623, 302, according as the diffusion tube is filled with hydrogen, with carbonic acid, or with chlorine gas. Now, if the air were rushing into a vacuum in all these cases, why should it not always enter it with the same velocity? Something more, therefore, must be assumed than that gases are vacua to each other, in order to explain the whole phenomena observed in diffusion.

Passage of gases through membranes.—In connexion with diffusion, the passage of gases through humid membranes may be noticed. If a bladder, half filled with air, with its mouth tied, be passed up into a large jar filled with carbonic acid gas, standing over water, the bladder, in the course of twenty-four hours, becomes greatly distended, by the insinuation of the carbonic acid through its substance, and may even burst, while a very little air escapes outwards from the bladder. But this is not simple diffusion. The result depends upon two circumstances: first, upon carbonic acid being a gas easily liquefied by the water in the substance of the membrane,—the carbonic acid penetrates the membrane as a liquid; secondly, this liquid is in the highest degree volatile, and, therefore, evaporates very rapidly from the inner surface of the bladder into the air confined in it. The air in the bladder comes to be expanded in the same manner as if ether or any other volatile fluid was admitted into it. The phenomenon was observed by Dalton in its simplest form. Into a very narrow jar, half filled with carbonic acid gas over water, he admitted a little air. The air and gas were accidentally separated by a water-bubble, and thus prevented from intermixing. But the carbonic gas immediately began to be liquified by the film of water, and passing through it, evaporated into the air below. The air was in this way gradually expanded, and the water-bubble ascended in the tube. Here the particular phenomenon in question was observed to take place, but without the intervention of membrane. It is to be remembered that the thinnest film of water or any liquid is absolutely impermeable to a gas as such.

In the experiments of Drs. Mitchell and Faust, and others, in which gases passed through a sheet of caoutchouc, it is to be supposed that the gases were always liquefied in that substance, and penetrated through it in a fluid form. Indeed, few bodies are more remarkable than caoutchouc for the avidity with which they imbibe various liquids. The absorption of ether, of naphtha, of oil of turpentine, softening the substance of the caoutchouc, without dissolving it, may be referred to. It is likewise always those gases which are more easily liquified by cold or pressure that pass most readily through both caoutchouc and humid membranes. Dr. Mitchell found that the time required for the passage of equal volumes of different gases through the same membrane, was

1	minute, with	ammonia.
2½	minutes, with	sulphuretted hydrogen.
3¼	"	cyanogen.
5½	"	carbonic acid.
6½	"	nitrous oxide.
27½	"	arsenietted hydrogen.
28	"	olefiant gas.
37½	"	hydrogen.
113	"	oxygen.
160	"	carbonic oxide.

and a much greater time with nitrogen.

DIFFUSION OF VAPOURS INTO AIR, OR SPONTANEOUS EVAPORATION.

Volatile bodies, such as water, rise into air as well as into a vacuum, and obviously according to the law by which gases diffuse through each other. Thus, if a small quantity of the volatile liquid ether be conveyed into two tall jars standing over water, one half filled with air, and the other with hydrogen gas, the air and hydrogen immediately begin to expand, from the ascent of the ether-vapour into them, and the two gases in the end have their volume increased exactly in the same proportion. But the hydrogen gas undergoes this expansion in half the time that the air requires;

that is to say, ether-vapour follows the usual law of diffusion in penetrating more rapidly through the lighter gas.

We are indebted to Dr. Dalton for the discovery that the evaporation of water has the same limit in air as in a vacuum. Indeed, the quantity of vapour from a volatile body which can rise into a confined space, is the same, whether that space be a vacuum, or be already filled with air or gas, in any state of rarefaction or condensation. The vapour rises, and adds its own elastic force, such as it exhibits in a vacuum, to the elastic force of the other gases or vapours already occupying the same space. Hence, it is only necessary to know what quantity of any vapour rises into a vacuum at any particular temperature; — the same quantity rises into air. Thus the vapour from water, which rises into a vacuum at 80°, depresses the mercurial column one inch, or its tension is one-thirtieth of the usual tension of the air. Now, if water at 80° be admitted into dry air, it will increase the tension of that air by 1-30th, if the air be confined; or increase its bulk by 1-30th, if the air be allowed to expand. M. Regnault has, indeed, observed that the tension of the vapour of water in air, and in pure nitrogen gas, is always a little more feeble (2 or 3 per cent.) than in a vacuum for the same temperature, (Annales de Ch. et Ph., xv. 137); from which may be inferred the existence of some physical obstacle to the full diffusion of vapours, of which the nature is at present unknown. The density of the vapour of water in air saturated with it may also be taken as the same as it has been found in a vacuum, or 622 (air = 1000), M. Regnault having observed it to deviate not more than one-hundredth part from that density, at all temperatures between 32° and 72° Fahr. — (Ibid., p. 160).

The spontaneous evaporation of water into air is much affected by three circumstances:—1. The previous state of dryness of the air — for a certain fixed quantity only of vapour can rise into air, as much as into the same space if vacuous; and if a portion of that quantity be already present, so much the less will be taken up by the air; and no evaporation whatever takes place into air which contains this fixed quantity, and is already saturated with humidity. 2. By warmth — for the higher the temperature the more considerable is the quantity of vapour which rises into any accessible space. Thus water emits so much vapour at 40° as expands the air in contact with it 1-114th part, and at 60° as much as expands air 1-57th part, or double the quantity emitted at the lower temperature. Hence, humid hot air contains a much greater portion of moisture than humid cold air. 4. The evaporation of water is greatly quickened by the removal of the incumbent air in proportion as it becomes saturated; and hence a current of air is exceedingly favourable to evaporation.

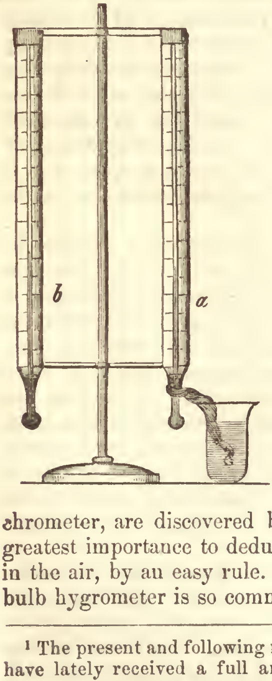
When air saturated with humidity at a high temperature is cooled, it ceases to be able to sustain the large portion of vapour which it possesses, and the excess assumes the liquid form, and precipitates in drops. Many familiar appearances depend upon the condensation of the vapour in the atmosphere. When a glass of cold water, for instance, is brought into a warm room, it is often quickly covered with moisture. The air in contact with the glass is chilled, and its power to retain vapour so much reduced as to occasion it to deposit a portion upon the cold glass. It is from the same cause that water is often seen in the morning running down in streams upon the inside of the glass panes of bed-room windows. The glass has the low temperature of the external air, and by contact cools the warm and humid air of the apartment so as to occasion the precipitation of its moisture. Hence also, when a warm thaw follows after frost, thick stone walls which continue to retain their low temperature are covered by a profusion of moisture.

Hygrometers. — As water evaporates at all temperatures, however low, the atmosphere cannot be supposed to be ever entirely destitute of moisture. The proportion present varies with the temperature, the direction of the wind, and other circumstances, but is generally greater in summer than in winter. There are various means by which the moisture in the air may be indicated, and its quantity estimated. affording principles for the construction of different hygroscopes or hygrometers.

1. The chemical method consists in passing a known measure of air over a highly hygrometric substance, such as chloride of calcium, contained in a glass tube, which has been weighed; the increase of weight is that of the vapour absorbed. The experiment admits of being made with rigorous accuracy, but is seldom had recourse to, except to check other methods which are more expeditious, but less certain.[1]

2. Many solid substances swell on imbibing moisture, and contract again on drying: such as wood, parchment, hair, and most dry organic substances. The hygrometer of Deluc consisted of an extremely thin piece of whalebone, which in expanding and contracting moved an index. The principle of this instrument is illustrated in the transparent shavings of whalebone cut into figures, which bend and crumple up when laid upon the warm hand. Saussure made use of human hair boiled in a solution of carbonate of soda, as a hygrometric body, and it appears to answer better than any other substance of the class. Regnault does not make any essential change in the construction of Saussure, but prefers to deprive the hairs of unctuous matter by leaving them for twenty-four hours in a tube filled with ether. They preserve in this way all their tenacity, and acquire at the same time nearly as much sensibility as if they had been prepared by an alkali. He finds that each instrument must be graduated experimentally by placing it in a confined space with air kept in a known state of humidity by the presence of dilute sulphuric acid of several degrees of strength, which he indicates, and supplies tables of their tension at different temperatures (Ann. de Ch., t. xv. p. 173). Of this instrument, which is so convenient in a great many circumstances, he speaks more highly than physicists generally of late, but at the same time remarks that it requires great circumspection in the observer, and that the occasional verification of the instrument by means of the solutions first employed in graduating it is indispensable.

Fig. 44.



3. The degree of dryness of the air may be judged of by the rapidity of evaporation. Leslie made use of his differential thermometer as a hygrometer, covering one of the bulbs with muslin, and keeping it constantly moist by means of a wet thread from a cup of water placed near it. The evaporation of the moisture cools the ball, and occasions the air in it to contract. This instrument gives useful information in regard to the rapidity of evaporation, or the drying power of the air, but does not indicate directly the quantity of moisture in the air. The *wet-bulb hygrometer*, more commonly used, acts on the same principle, but consists of two similar and very delicate mercurial thermometers, the bulb of one of which (*a*) is kept constantly moist, while the bulb of the other (*b*) is dry. The wet thermometer always indicates a lower temperature than the dry one, unless when the air is fully saturated with moisture, and no evaporation from the moist bulb takes place. In making an observation, the instrument is generally placed, not in absolutely still air, but in an open window where there is a slight draught.

The indications of the wet-bulb hygrometer, or psychrometer, are discovered by simple inspection. It is, therefore, a problem of the greatest importance to deduce from them the dew point, or the tension of the vapour in the air, by an easy rule. Could this inference be made with certainty, the wet-bulb hygrometer is so commodious that it would supersede all others. I shall place

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[1] The present and following methods of hygrometry, and all the experimental data required, have lately received a full and critical revision from M. Regnault, of the greatest value. See his "Etudes sur l'Hygrometrie," Annales de Chimie, &c., 1835, 3 sér. t. xv. p. 129.

below a formula for this purpose, which has been used for several years in the north of Europe, and the same as it has been recently modified.[1]

4. The most simple mode of ascertaining the absolute quantity of vapour in the air is to cool the air gradually, and note the degree of temperature at which it begins to deposit moisture, or ceases to be capable of sustaining the whole quantity of vapour which it possesses. The air is saturated with vapour for this particular degree of temperature, which is called its *dew-point.* The saturating quantity of vapour for the degree of temperature indicated may then be learned by reference to a table of the tension of the vapour of water at different temperatures.[2] It is the absolute quantity of vapour which the air at the time of the observation possesses. The dew-point may be ascertained most accurately by exposing to the air a thin cup of silver or tin-plate containing water so cold as to occasion the condensation of dew upon the metallic surface. The water in the cup is stirred with the bulb of a small thermometer, and as the temperature gradually rises, the degree is noted at which the dew disappears from the surface of the vessel. The temperature at which this occurs may be taken as the dew-point. Water may generally be cooled sufficiently in summer to answer for an experiment of this kind by dissolving pounded sal-ammoniac in it.

The dew-point may be observed much more quickly by means of the elegant hygrometer of the late Mr. Daniell. (Daniell's Meteorological Essays, p. 147). This instrument (see figure 45) consists of two glass balls, *a* and *b*, connected by a syphon, and containing a quantity of ether, from which the air has been expelled by the same means as in the cryophorus of Dr. Wollaston (page 75). One of the arms of the syphon tube contains a small thermometer, with its scale, which should be of white enamel; the bulb of the thermometer descends into the ball, *b*, at the extremity of this arm, and is placed, not in the centre of the ball, but as near as possible to some point of its circumference. A zone of this ball is gilt and burnished, so that the deposition of dew may easily be perceived upon it. The other ball, *a*, is covered with muslin. When an observation is to be made, this last ball is moistened with ether, which is supplied slowly by a drop or two at a time. It is cooled by the evaporation of the ether, and becomes capable of condensing the vapour of the included fluid, and thereby occasions evaporation in the opposite ball, *b*, containing the thermometer. The temperature of the ball, *b*, should be thus

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[1] The psychrometer was first suggested by Gay-Lussac (Annales de Chimie, &c., t. xxi. p. 91), and its application particularly studied by Dr. E. H. August, of Berlin, (*Ueber die Fortschritte der Hygrometrie*), 1830, and Dr. Apjohn (Philosophical Magazine, 1838, &c.) To obtain the tension of vapour in the atmosphere from the two temperatures observed, the following formula is given by Dr. August, neglecting some very small quantities:—

$$x = f' - \frac{0.568\,(t - t')}{640 - t'} .\, h;$$

where t and t' are temperatures (Centigrade) of the dry and wet thermometers, f' the tension of vapour in air saturated at the temperature t', h the height of the barometer, and $640 - t'$ the latent heat of aqueous vapour. Some of the numerical data are modified by M. Regnault, and the formula becomes:—

$$x = f' - \frac{0.429\,(t - t')}{610 - t'} .\, h;$$

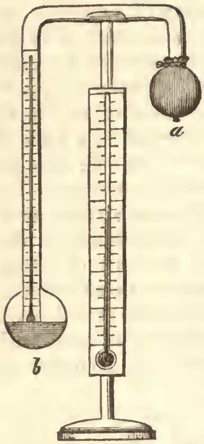
Or,

$$x = f' - \frac{0.480\,(t - t')}{616 - t} ,\, h.$$

The last co-efficient 0.480 he finds to give a coincidence almost perfect between the calculated and true results, when the air is not more than four-tenths saturated. Otherwise the first coefficient 0.429 is least objectionable. (Annales, &c., xv. pp. 202 and 226).

[2] A table by M. Regnault for this purpose will be given in an Appendix. [*See Supplement*, p. 646.]

Fig. 45.



reduced in a gradual manner, so that the degree of the thermometer at which dew begins to be deposited on the metallic part of the surface of the ball may be observed with precision. The temperature of *b* being thereafter allowed to rise, the degree at which the dew disappears from its surface may likewise be noted. It should not differ much from the temperature of the deposition, and will probably give the dew-point more correctly; although, strictly speaking, the mean between the two observations should be the true dew-point. It is convenient to have a second thermometer in the pillar of the instrument, for observing the temperature of the air at the time.

M. Regnault proposes a modification of Daniell's hygrometer, under the name of the *Condenser-hygrometer*, (Annales de Chimie, et Ph. t. xv. Pl. 2), which appears to be the most perfect instrument of the class. It consists of a thimble, *a b c*, (figure 46), made of silver, very thin, and perfectly polished, 1-8 inch in depth, and 8-10ths of an inch in diameter, which is fitted tightly upon a glass tube, *c d*, open at both ends. The tube has a small lateral tubulure, *t* The upper opening of the tube is closed by a cork, which is traversed by the stem of a very sensible thermometer occupying its axis; the bulb of the thermometer is in the centre of the silver thimble. A very thin glass tube, *f g*, open at both ends, traverses the same cork, and descends to the bottom of the thimble. Ether is poured into the tube as high as *m n*, and the tubulure *t* is placed in communication by means of a leaden tube with an aspirator jar six or eight pints in capacity, filled with water. The aspirator jar is placed near the observer, while the condenser-hygrometer is kept as far from his person as is desirable.

Fig. 46.

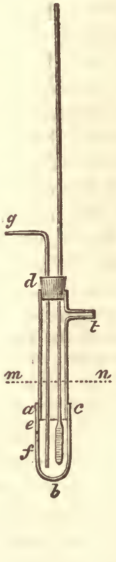
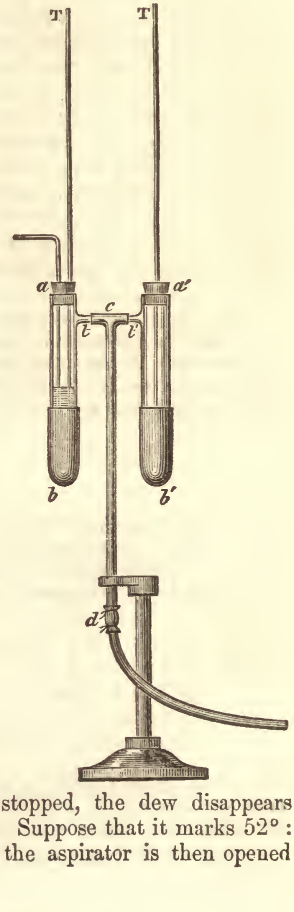


Fig. 47.



On allowing water to run from the aspirator jar, air enters by the tube *g f*, passing bubble by bubble through the ether, which it cools by carrying away vapour; the refrigeration is the more rapid, the more freely the water is allowed to flow; and the whole mass of ether presents a sensibly uniform temperature, as it is briskly agitated by the passage of the bubbles of air. The temperature is sufficiently lowered in less than a minute to determine an abundant deposit of dew. The thermometer is then observed through a little telescope; suppose that it is read off at 50°. This temperature is evidently somewhat lower than what corresponds exactly to the air's humidity. By closing the stopcock of the aspirator the passage of air is stopped, the dew disappears in a few seconds, and the thermometer again rises. Suppose that it marks 52°: this degree is above the dew-point. The stopcock of the aspirator is then opened very slightly, so as to determine the passage of a very small stream of air bubbles through the ether. If the thermometer continues, notwithstanding, to rise, the stopcock is opened further, and the thermometer brought down to 51°.8: by shutting the stopcock slightly, it is easy to stop the falling range, and make the thermometer remain stationary at 51°.8 as long as is desired. If no dew forms after the lapse of a few seconds, it is evident that 51°.8 is higher than the dew-point. It is brought down to 51°.6, and maintained there by regulating the flow. The metallic surface being now observed to become dim after a few seconds, it is concluded that 51°.6 is too low, while 51°.8 was too high. A still greater approximation even may be made, by now finding whether 51°.7 is above or below the point of condensation. These operations may be executed in a very short time, after a little practice; three or four minutes being found sufficient, by M. Regnault, to determine the dew-point to within about $\frac{1}{10}$th of a degree Fahr. A more considerable fall of temperature may be obtained by means of this than the original instrument of Daniell, with the consumption of a much less quantity of ether; indeed, that liquid may be dispensed with entirely, and alcohol substituted for it. The thermometer, T, to observe the temperature of the air during the experiment, is placed in a second similar glass tube and thimble *a′ b′*, also under the influence of the aspirator, but containing no ether.

In evaporating by means of hot air, as in drying goods in the ordinary bleachers' stove, which is heated by flues from a fire carried along the floor, it should be kept in mind that a certain time must elapse before air is saturated with humidity. Mr. Daniell has observed that a few cubic inches of dry air continue to expand for an hour or two, when exposed to water at the temperature of the air. At high temperatures, the diffusion of vapour into air is more rapid; but still it is not at all instantaneous. Hence, in such a drying stove, means ought to be taken to repress rather than to promote the exit of the hot air; otherwise a loss of heat will be occasioned by the escape of the air, before it is saturated with humidity. The greatest advantage has been derived from closing such a stove as perfectly as possible at the top, and only opening it after the goods are dried and about to be removed, in order to allow of a renewal of the air in the chamber between each operation. In evaporating water by heated air, the vapour itself carries off exactly the same quantity of heat as if it were produced by boiling the water at 212°, while the air associated with it likewise requires to have its temperature raised, and therefore occasions an additional consumption of heat. Hence water can never be evaporated by air in a drying stove with so small an expenditure of fuel as in a close boiler.

When bodies to be dried do not part with their moisture freely, but in a gradual manner, as is the case with roots, and most organic substances, the hot air to dry them may be greatly economised by a particular mode of applying it, which is practised in the madder-stove. The principle of this drying stove is illustrated by the annexed figure, in which *a b* represent a tight chamber, having two openings, one near the roof, by which hot air is admitted into the chamber, and another at the bottom, by which the air escapes into the tall chimney *c*. The chamber contains a series of stages, from the floor to the roof, on the lowest of which, sacks, half filled with the damp madder roots, are first placed. In proportion as the roots dry, the bags are raised from stage to stage, till they arrive at the highest stage, where they are exposed to the air when hottest and most desiccating. As the dried roots are removed from the top, new roots are introduced below, and passed through in the same manner. Here the dry and

Fig. 48.

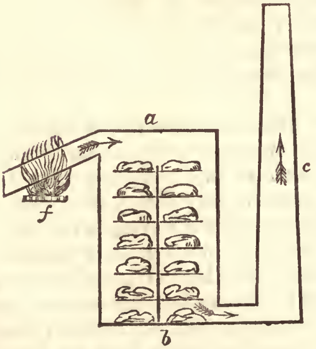
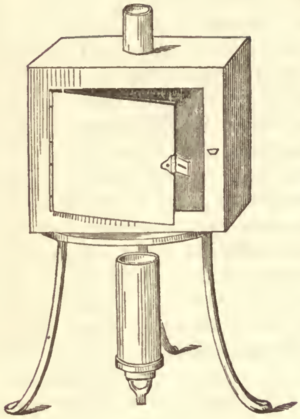


FIG. 49.



hot air, after taking all the moisture which the roots on the highest stage will part with, descends, and is still capable of abstracting a second quantity of moisture from the roots on the next, and so on, as it proceeds, till it passes away into the chimney absolutely saturated with moisture, after having reached the bottom of the chamber.

It is frequently an object to dry a small quantity of a substance most completely (such as an organic substance for analysis) at some steady temperature, such as 212°. This is effected very conveniently by means of a little oven, (figure 49), consisting of a double box of copper or tin-plate, about six inches square, with water between the casings, which is kept in a state of ebullition by means of a gas flame, or spirit lamp.

NATURE OF HEAT.

It is convenient to adopt the material theory of heat in considering its accumulation in bodies, and in expressing quantities of heat and the relative capacities of bodies for heat. Indeed, every thing relating to the absorption of heat suggests the idea of its substantial existence; for heat, unlike light, is never extinguished when it falls upon a body, but is either reflected and may be farther traced, or is absorbed and accumulated in the body, and may again be derived from it without loss. But the mechanical phenomena of heat, which resemble those of light, may be explained with equal if not greater advantage by assuming an undulatory theory of heat, corresponding with the undulatory theory of light. A peculiar imponderable medium or ether is supposed to pervade all space, through which undulations are propagated that produce the impression of heat. A hot radiant body is a body possessing the faculty to originate or excite such undulations in the ether or medium of heat, which spread on all sides around it, like the waves from a pebble thrown into still water. Sound is propagated by waves in this manner, but the medium in which they are generally produced, or the usual vehicle of sound, is the air; and all the experiments on the reflection and concentration of heat, by concave reflectors, may be imitated by means of sound. Thus, if a watch instead of the lamp be placed in the focus of one of a pair of conjugate reflecting mirrors (fig. 20, p. 54), the waves of air occasioned by its beating emanate from the focus, strike against the mirror, and are reflected from it, so as to break upon the face of the opposite mirror, are concentrated into its focus, and communicate the impression of sound to an ear placed there to receive it. The transmission of heat from the focus of one mirror to the focus of the other may easily be conceived to be the propagation of similar undulations through another and different medium from air, but coexisting in the same space.

In adopting the material theory of heat, we are under the necessity of assuming that there are different kinds of heat, some of which are capable of passing through glass, such as the heat of the sun, while others, such as that radiating from the hand, are entirely intercepted by glass. But on the undulatory theory the different properties of heat are referred to differences in the size of the waves, as the differences of colour are accounted for in light. Heat of the higher degrees of intensity, however, admits of a kind of degradation, or conversion into heat of lower intensity, to which we have nothing parallel in the case of light. Thus when the calorific rays of the sun, which are of the highest intensity, pass through glass, and strike a black wall, they are absorbed, and appear immediately afterwards radiating from the heated wall, as heat of low intensity, and are no longer capable of passing through glass.

It is as yet an unsolved problem to reverse the order of this change, and convert heat of low into heat of high intensity. The same degradation of heat or loss of intensity, is observed in condensing steam in distillation. The whole heat of the steam, both latent and sensible, is transferred without loss in that process, to perhaps fifteen times as much condensing water; but the intensity of the heat is reduced from 212° to perhaps 100° Fahr. The heat is not lost; for the fifteen parts of water at 100° are capable of melting as much ice as the original steam. But by no quantity of this heat at 100° can temperature be raised above that degree: no means are known of giving it intensity.

If heat of low is ever changed into heat of high intensity, it is in the compression of gaseous bodies by mechanical means. Let steam of half the tension of the atmosphere, produced at 180°, in a space otherwise vacuous, be reduced into half its volume, by doubling the pressure upon it, and its temperature will rise to 212°. If the pressure be again doubled, the temperature will become 250°, and the whole latent heat of the steam will now possess that high intensity. When air itself is rapidly compressed in a common syringe, we have a remarkable conversion of heat of low into heat of very high intensity.

It may be imagined that the elevation of temperature produced in the friction of hard bodies has a similar origin; that it results from the conversion of heat of low intensity, which the bodies rubbed together possess, into heat of high intensity. But it would be necessary further to suppose that a supply of heat of low intensity to the bodies rubbed can be endlessly kept up, by conduction or radiation, from contiguous bodies, as there is certainly no limit to the production of heat by means of friction.*

Count Rumford, by boring a cylinder of cast iron, raised the temperature of several pounds of cold water to the boiling point. Sir H. Davy succeeded in melting two pieces of ice in the vacuum of an air-pump, by making them rub against each other, while the temperature of the air-pump itself and the surrounding atmosphere was below 32°. M. Haldot observed that when the surface of the rubber was rough, only half as much heat appeared as when the rubber was smooth. When the pressure of the rubber was quadrupled, the proportion of heat evolved was increased seven-fold. When the rubbing apparatus was surrounded by bad conductors of heat, or by non-conductors of electricity, the quantity of heat evolved was diminished. (Nicholson's Journal, xxvi. 30).

According to Pictet, a piece of brass, rubbed with a piece of cedar wood, produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were rubbed together. He also finds that solids alone produce heat by friction; no heat appears to arise from the friction of one liquid upon another liquid, or upon a solid, nor by the friction of a current of air or gas upon a liquid or solid.

One other point only connected with the nature of heat remains, to which there is at present occasion to allude—the existence of a repulsive property in heat. Such a repulsive power in heated bodies is inferred to exist from the appearance of extreme mobility which many fine powders assume, such as precipitated silica, on being heated nearly to redness. Professor Forbes also attributes to such a repulsion the vibrations which take place between metals unequally heated, and the production of tones, to which allusion has already been made. But this repulsive power was rendered conspicuous, and even measurable, by Dr. Baden Powell, in the case of glass lenses, of very slight convexity, pressed together. On the application of heat, a separation of the glasses, through extremely small but finite spaces, was indicated by a change in the tints which appear between the lenses, and which depend upon the thickness of the included plate of air. This repulsion between heated surfaces appears to be promoted by whatever tends to the more rapid communication of heat. (Phil. Trans. 1834, p. 485).

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* [*See Supplement*, p. 652.]

CHAPTER II.

LIGHT.

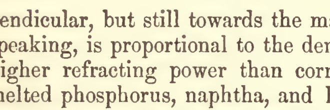
THE mechanical properties of light constitute the science of optics, and belong, therefore, to physics, and not to chemistry. But it may be useful, by a short recapitulation, to recal them to the memory of the reader.

1. The rays of light emanate with so great velocity from the sun, that they occupy only 7½ minutes in traversing the immense space which separates the earth from that luminary. They travel at the rate of 192,500 miles in a second, and would, therefore, move through a space equal to the circumference of our globe in 1-8th of a second. They are propagated continually in straight lines, and spread or diverge at the same time; so that their density diminishes in the direct proportion of the squares of their distance from the sun. Hence, if the earth were at double its present distance from the sun, it would receive only one-fourth of the light; at three times its present distance, one-ninth; at four times its present distance, one-sixteenth, &c.

2. When the solar rays impinge upon a body, they are reflected from its surface, and bound off, as an elastic ball striking against the same surface in the same direction would do; or they are absorbed by the body upon which they fall, and disappear, being extinguished; or lastly, they pass through the body, which in that case is transparent or diaphanous. In the first case, the body becomes visible, appearing white, or of some particular colour, and we see it in the direction in which the rays reach the eye. In the second case, the body is invisible, no light proceeding from it to the eye; or it appears black, if the surrounding objects are illuminated. In the third case, if the body be absolutely transparent, it is invisible, and we see through it the object from which the light was last reflected. But light is often greatly affected in passing through transparent bodies.

3. If light enter such media, of uniform density, perpendicularly to their surface, its direction is not altered; but in passing obliquely out of one medium into another, it undergoes a change of direction. If the second medium be denser than the first, the ray of light is bent, or *refracted*, nearer to the perpendicular; but in passing out from a denser into a rarer medium, it is refracted from the perpendicular. Thus, when the ray of light *r*, passing through the air, falls obliquely upon a plate of glass at the point *a*, instead of continuing to move in the same straight line *a b*, it is bent towards the perpendicular at *a*, and proceeds in the direction *a c*. The ray is bent to the side on which there is the greatest mass of glass. On passing out from the glass into the air, a rarer medium, at the point *c*, the ray has its direction again changed, and in this case *from* the perpendicular, but still towards the mass of glass. The amount of refraction, generally speaking, is proportional to the density of a body, but combustible bodies possess a higher refracting power than corresponds to their density. Hence the diamond, melted phosphorus, naphtha, and hydrogen gas, exhibit this effect upon light in a greater degree than other transparent bodies. Dr. Wollaston had recourse to this refracting power as a test of the purity of some substances. Thus, genuine oil of cloves had a refracting power expressed by the number 1535, while that of an impure specimen was not more than 1498.

FIG. 50.



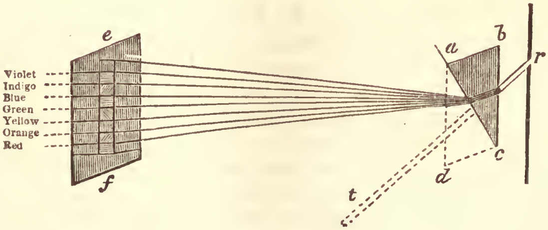
4. In passing through many crystallized bodies, such as Iceland spar, a certain portion of light is refracted in the usual way, and another portion undergoes an

extraordinary refraction, in a plane parallel to the diagonal which joins the two obtuse angles of the crystal. Such bodies are said to *refract doubly*, and exhibit a double image of any body viewed through them.

5. Reflected and likewise doubly refracted light assume new properties. *Common* light, by being reflected from the surface of glass, or any bright surface non-metallic, is more or less of it converted into what is called *polarized* light. If it be reflected at one particular angle of incidence, 56°.45′, it is *all* changed into polarized light; and the further the angle of reflection deviates from 56°, on either side, the less is polarized, and the more remains common light. 56° is the maximum polarizing angle for glass; 52°.45′ for water. The light is said to be *polarized*, from certain properties which it assumes, which seem to indicate that the ray, like a magnetic bar, has sides in which reside peculiar powers. One of these new properties is, that when it falls upon a second glass plate, it is not reflected in the same way as common light. If the plane of the second reflector is *perpendicular* to the first, and the ray fall at an angle of 56°, it is not reflected at all, it *vanishes;* but if *parallel*, it is entirely reflected. Polarized light appears to possess some most extraordinary properties, in regard to vision, of useful application. It is said that a body which is quite transparent to the eye, and which appears upon examination to be as homogeneous in its structure as it is in its aspect, will yet exhibit, under polarized light, the most exquisite organization. As an example of the utility of this agent in exploring mineral, vegetable, and animal structures, Sir D. Brewster refers to the extraordinary structure of the minerals apophyllite and analcime; to the symmetrical and figurate disposition of siliceous crystals in the epidermis of equisetaceous plants, and to the wonderful variations of density in the crystalline lenses, and the integuments of the eyes of animals, which polarized light renders visible. (Rep. of the British Association, vol. i. Report upon Optics, by Sir. D. Brewster.)

6. *Decomposition of light.*— When a beam of light from the sun is admitted into a dark room, by a small aperture *r* in a window-shutter, and is intercepted in its passage by a wedge or solid angle of glass *a b c*, it is refracted as it enters, and a second time as it issues from the glass; and instead of forming a round spot of white light, as it would have done if allowed to proceed in its original direction *r t*, it illuminates with several colours an oblong space of a white card *e f*, properly placed to receive it. The solid wedge of glass is called a prism, and the oblong coloured image on the card, the solar spectrum. Newton counted seven bands of different colours in the spectrum, which, as they succeed each other from the upper part of the spectrum represented in the figure, are violet, indigo, blue, green, yellow, orange, and red. The beam of light admitted by the aperture in the window-shutter has been separated in passing through the prism into rays of different colours, and this separation obviously depends upon the rays being unequally refrangible. The blue rays are more considerably refracted or deflected out of their course, in passing through the glass, than the yellow rays, and the yellow rays than the red. Hence the violet end is spoken of as the most refrangible, and the red as the least refrangible end of the spectrum.

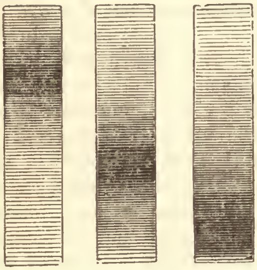
FIG. 51.



The coloured bands of the spectrum differ in width, and are shaded into each other; and it is not to be supposed that there are really rays of seven different colours. Sir D. Brewster has established, in his analysis of solar light, that there are rays of three colours only, blue, yellow, and red, which were well known to artists to be the three primary colours of which all others are compounded.

A certain quantity of white light, and a portion of each of the primary rays, may be found at every point from the top to the bottom of the spectrum. But each of the primary rays predominates at a particular part of the spectrum. This point is, for the blue rays, near the top of the spectrum; for the yellow rays, somewhat below the middle; and for the red rays, near the bottom of the spectrum. Hence, there exist rays of each colour of every degree of refrangibility; but the great proportion of the yellow rays is more refrangible than the red, and the great proportion of the blue more refrangible than either the yellow or red. The compound spectrum which we observe is in fact produced by the superposition of three simple spectra, a blue, a yellow, and a red spectrum. The distribution of the rays in each of these simple spectra is represented by the shading in the annexed figures. Of the seven different coloured bands into which Newton divided the spectrum, not one is a pure colour. The orange is produced by a predominance of the yellow and red rays; the green, by the yellow and blue rays, and the indigo and violet are essentially blue, with different proportions of red and yellow.[1]

FIG. 52.


Blue spectrum. Yellow spectrum. Red spectrum.

By placing a second prism *a d c*, in a reversed position, in contact with the first prism, the colours disappear, and we have a spot of white light, as if both prisms were absent. The three coloured rays of the spectrum, therefore, produce white light by their union.

On examining the solar spectrum, Dr. Thomas Young observed that it is crossed by several dark lines; that is, that there are interruptions in the spectrum, where there is no light of any colour. Fraunhofer subsequently found that the lines in the spectrum of solar light were much more numerous than Dr. Young had imagined, while the spectrum of *artificial* white flames contains all the rays which are thus wanting. One of the most notable is a double dark line in the yellow, which occurs in the light of the sun, moon, and planets. In the light of the fixed stars, Sirius and Castor, the same double line does not occur; but one conspicuous dark line in the yellow, and two in the blue. The spectrum of Pollux, on the contrary, is the same as that of the sun. Now a very recent discovery of Sir D. Brewster has given these observations an entirely chemical character. He has found that the white light of ordinary flames requires merely to be sent through a certain gaseous medium (nitrous acid vapour) to acquire more than a thousand dark lines in its spectrum. He is hence led to infer that it is the presence of certain gases in the atmosphere of the sun which occasions the observed deficiencies in the solar spectrum. We may thus have it yet in our power to study the nature of the combustion which lights up the suns of other systems. Dr. Miller, by subjecting the spectrum to the absorptive influences of chlorine, iodine, bromine, perchloride of manganese, and other coloured vapours, brought into view numerous dark bands not previously observed. The spectra of coloured flames were also marked by peculiar lines.

The rays of *heat* are distributed very unequally throughout the luminous spectrum; most heat being found associated with the red or least refrangible luminous rays, and

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[1] Sir David Brewster, On a New Analysis of the Solar Light, indicating three primary colours, forming coincident spectra of equal length. Edinburgh Phil. Trans. vol. xii. p. 123.

least with the violet rays. Indeed, when the solar beam is decomposed by a prism of a highly diathermanous material, such as rock salt, the rays of heat are found to extend, and to have their point of maximum intensity considerably beyond the visible spectrum, on the side of the red ray. Hence, although there are calorific rays of all degrees of refrangibility, the great proportion of them are even less refrangible than the least refrangible luminous rays. It is to be observed that the least refrangible rays are absorbed in greatest proportion in passing through bodies which are not highly diathermanous; such as crown-glass, and water. Hence prisms of these substances, allowing only the more refrangible rays of heat to pass, give a spectrum which is hottest in the red, or perhaps even in the yellow ray, and possesses little or no heat beyond the border of the red ray. The inequality in refrangibility existing between the rays of heat and of light is decisive of the fact that they are peculiar rays, that can be separated, although associated together in the sunbeam. Indeed, Melloni finds that light from both solar and terrestrial sources is divested of all heat by passing successively through water, and a glass coloured green by oxide of copper, being incapable as it issues from these media of affecting the most delicate thermoscope.

The light of the sun is capable of inducing certain chemical changes which depend neither upon its luminous nor calorific rays, but upon the presence of what are called *chemical rays*. Thus, under the influence of light, chlorine gas is capable of decomposing water, combining with its hydrogen, and liberating oxygen; the chlorine in the freshly precipitated chloride of silver appears to be liberated, and the colour of the salt changes from white to black from the formation of a subchloride. Photographic impressions are obtained on paper by means of this and other salts of silver, particularly the bromide and iodide, which are still more sensitive to light. A polished plate of silver, covered with the thinnest film of iodide, is employed to receive the image in the daguerréotype. The moist chloride of silver is darkened more rapidly by the violet than by the red rays of the spectrum; but this change is produced upon it even when carried a little way out of the visible spectrum on the side of the violet ray. The rays found in that situation are, therefore, more refrangible than any other kind of rays in the spectrum. Their characteristic effect is to promote those chemical decompositions in which oxygen is withdrawn from water and other oxides; and hence they are sometimes named *de-oxidizing* rays. These rays were likewise supposed to communicate magnetism to steel needles exposed to them; but this opinion is no longer tenable.

[The subjects of Polarization and the Chemical Action of Light will be found in the *Supplement*, p. 658.]

CHAPTER III.

SECTION I.

CHEMICAL NOMENCLATURE AND NOTATION.

THERE are fifty-nine substances at present known, which are simple, or contain one kind of matter only. Their names are given in the following table, together with certain useful numbers which express the quantities by weight, according to which the different elements combine with each other. The letter or symbol annexed to the name is employed to represent these particular quantities of the elements, or the chemical equivalents.

TABLE OF ELEMENTARY SUBSTANCES,

WITH THEIR CHEMICAL EQUIVALENTS.

*** For the *authorities* for the *numbers* in this table, see note at page 104.

Names of Elements.	Symbols.	Equivalents.		
		Hydrogen =1.	Oxy.=100. H.=12·5.	
Aluminum	Al	13·69	171·17	Al_2O_3, alumina. Al_2Cl_3, chloride of aluminum. Al_2O_3, $3SO_3$, sulphate of alumina.
Antimony (Stibium)........	Sb	129·03	1612·90	SbO_3, oxide of antimony. SbO_5, antimonic acid.
Arsenic	As	75	937·50	AsO_3, arsenious acid. AsO_5, arsenic acid.
Barium	Ba	68·64	858·01	BaO, baryta. $BaCl$, chloride of barium.
Bismuth.............	Bi	70·95	886·92	BiO, oxide of bismuth. BiO, NO_5, nitrate of bismuth. $BiCl$, chloride of bismuth.
Boron................	B	10·90	136·20	BO_3, boric or boracic acid. BFl_3, fluoboric acid.
Bromine.............	Br	78·26	978·30	BrO_5, bromic acid. BrH, hydrobromic acid.
Cadmium............	Cd	55·74	696·77	CdO, oxide of cadmium. CdS, sulphide or sulphuret of cadmium.
Calcium	Ca	20	250·00	CaO, lime. $CaCl$, chloride of calcium.
Carbon...............	C	6	75·00	CO, carbonic oxide. CO_2, carbonic acid. CS_2, sulphide or sulphuret of carbon.
Cerium	Ce	46	575	CeO, oxide of cerium. Ce_2O_3, sesquioxide of cerium.
Chlorine............	Cl	35·50	443·75	ClO_5, chloric acid. ClO_7, perchloric acid. ClH, hydrochloric acid.
Chromium	Cr	28·15	351·82	CrO_3, chromic acid. Cr_2O_3, sesquioxide of chromium. Cr_2O_3, $3SO_3$, sulphate of chromium.
Cobalt	Co	29·52	368·99	CoO, oxide of cobalt. Co_2O_3, sesquioxide of cobalt.
Copper (Cuprum).	Cu	31·66	395·70	Cu_2O, suboxide of copper. CuO, oxide of copper. CuO, SO_3, sulphate of copper.
Didymium	D	49·6	620	
Fluorine............	F	18·70	233·80	HF, hydrofluoric acid. BF_3, fluoboric acid.
Glucinum	Gl	26·50	331·26	Gl_2O_3, glucina. Gl_2Cl_3, chloride of glucinum.
Gold (Aurum)......	Au	98·33	1229·16	Au_2O. oxide of gold. Au_2O_3, sesquioxide of gold.
Hydrogen...........	H	1	12·50	HO, water. HO_2, binoxide of hydrogen.
Iodine................	I	126·36	1579·50	IO, iodic acid. HI, hydriodic acid.
Iridium	Ir	98·68	1233·50	IrO, protoxide of iridium. Ir_2O_3, sesquioxide of iridium.
Iron (Ferrum).....	Fe	28	350·00	FeO, protoxide of iron. Fe_2O_3, sesquioxide of iron. Fe_2O_3, $3SO_3$, sulphate of sesquioxide of iron.
Lanthanum.........	Ln	48	600	LnO, oxide of lanthanum.

Name of Elements.	Symbols.	Equivalents.		
		Hydrogen =1.	Oxy.=100. H.=12·5.	
Lead (Plumbum)	Pb	103·56	1294·50	PbO, oxide of lead. $PbCl$, chloride of lead.
Lithium	Li	6·43	80·37	LiO, oxide of lithium. $LiCl$, chloride of lithium.
Magnesium	Mg	12·67	158·35	MgO, magnesia. $MgCl$, chloride of magnesium.
Manganese	Mn	27·67	345·90	MnO, protoxide of manganese. MnO_2, binoxide of manganese. MnO_3, manganic acid. Mn_2O_7, permanganic acid.
Mercury (Hydrargyrum)	Hg	100·07	1250·9	Hg_2O, suboxide (black oxide). HgO, oxide (red oxide). Hg_2Cl, subchloride (calomel). $HgCl$, chloride (sublimate).
Molybdenum	Mo	47·88	598·52	MO_3, molybdic acid.
Nickel	Ni	29·57	369·68	NiO, protoxide of nickel. Ni_2O_3, sesquioxide of nickel.
Niobium	...	......	......	
Nitrogen or azote.	N (or Az)	14	175·00	NO_5, nitric acid. NO_2, binoxide of nitrogen. NH_3, ammonia.
Osmium	Os	99·56	1244·49	OsO_4, osmic acid.
Oxygen	O	8	100·00	
Palladium	Pd	53·27	665·90	PdO, protoxide of palladium. PdO_2, peroxide of palladium.
Pelopium	...	......	......	
Phosphorus	P	32·02	400·3	PO_5, phosphoric acid. PO_3, phosphorous acid. PH_3, phosphuretted hydrogen.
Platinum	Pt	98·68	1233·50	PtO, protoxide of platinum. PtO_2, binoxide of platinum.
Potassium (Kalium)	K	39·00	487·50	KO, potassa. KCl, chloride of potassium.
Rhodium	R	52·11	651·39	RO, protoxide of rhodium. R_2O_3, sesquioxide of rhodium.
Ruthenium	Ru	52·11	651·39	Ru_2O_3, sesquioxide of ruthenium.
Selenium	Se	39·57	494·58	SeO_3, selenic acid. SeH, hydroselenic acid.
Silicium	Si	21·35	266·82	SiO_3, silicic acid, or silica. SiF_3, fluosilicic acid.
Silver (Argentum)	Ag	108·00	1350·00	AgO, oxide of silver. $AgCl$, chloride of silver.
Sodium (Natronium)	Na	22·97	287·17	NaO, soda. $NaCl$, chloride of sodium.
Strontium	Sr	43·84	548·02	SrO, strontium. $SrCl$, chloride of strontium.
Sulphur	S	16	200·00	SO_3, sulphuric acid. SH, hydrosulphuric acid.
Tantalum or Columbium	Ta	92·30	1153·72	TaO, oxide of tantalum. TaO_3, tantalic acid.
Telurium	Te	66·14	801·76	TeO_3, telluric acid. TeH, hydrotelluric acid.
Thorium	Th	59·59	744·90	ThO, oxide of thorium. $ThCl$, chloride of thorium.
Tin (Stannum)	Sn	58·82	735·29	SnO, protoxide of tin. SnO_2, binoxide of tin.
Titanium	Ti	24·29	303·66	TiO_2, titanic acid. $TiCl_2$, bichloride of titanium.

Name of Elements.	Symbols.	Equivalents.		
		Hydrogen =1.	Oxy.=100. H.=12·5.	
Tungsten (Wolfram)........	W	94·64	1183·00	WO_3, tungstic acid.
Uranium	U	60	750	UO, oxide of uranium (urane of Peligot.) U_2O_3, uranic acid.
Vanadium..........	V	68·55	856·89	VO_3, vanadic acid.
Yttrium..............	Y	32·20	402·51	YO, yttria. YCl, chloride of yttrium.
Zinc	Zn	32·52	406·59	ZnO, oxide of zinc. ZnCl, chloride of zinc.
Zirconium..........	Zr	33·62	420·20	Zr_2O_3, zirconia. Zr_2Cl_3, chloride of zirconium.

⁂ The numbers in the preceding table are, with several exceptions, those of Berzelius. The equivalent of carbon has lately been reduced, with the general concurrence of chemists, from 76·44, on the oxygen scale, to 75, and hydrogen made 12·5 exactly, chiefly from the experiments of M. Dumas on the combustion of carbon and hydrogen gas by means of oxygen and oxide of copper, in his refined arrangement for organic analysis (Ann. de Chimie, 3 sér. t. i. p. 5). For nitrogen, M. Pelouze obtained, by two analyses of sal-ammoniac, the numbers 175·58 and 174·78; M. Marignac obtained for the same element the number 175·25, from the analysis of nitrate of silver; and Dr. T. Anderson has been led to nearly the same result, by an analysis of the nitrate of lead. These results permit the adoption of 175 as the equivalent of nitrogen: the old number was 177·04.

The equivalents of chlorine, potassium, and silver, the most fundamental numbers in the table, which were determined by Berzelius with remarkable precision, have received small corrections from M. Marignac. Seven experiments were made by the latter chemist on the decomposition of chlorate of potash by heat, in each of which from 800 to 1100 grains of the salt were employed, which gave him from 39.155 to 39.167 per cent. of oxygen; he adopts 39.161, the actual result of two experiments. Berzelius had obtained, thirty years before, 39.15. Pelouze has also obtained identically the same result (Poggendorff's Annalen, lviii. 171). On the other hand, 100 parts of silver required for precipitation from solution of nitrate, 69.062 parts of chloride of potassium (mean of six experiments); the maximum was 69.067, and the minimum 69.049; while the precipitated chloride of silver amounted after fusion to 132.84 parts, as the mean of five experiments, of which the maximum was 132.844, and the minimum 132.825 parts (Marignac). These experiments, from which the equivalents are deduced, obtain the unqualified approbation of Berzelius, who gives the numbers reduced to equivalents as they appear below. (Rapport Annuel sur le Progrès de la Chimie, par J. Berzelius, Paris, 1845, p. 32).

	Marignac.	Berzelius (old numbers).
Chlorine	443.20	442.65
Potassium	488.94	489.92
Silver	1349.01	1351.61

Finally, M. Maumené has investigated the same three important equivalents; decomposing the chlorate of potash by heat, and by guarding against certain minute sources of inaccuracy, raising the proportion of oxygen from 100 salt to 39.209; also decomposing the fused chloride of silver by hydrogen gas, and analyzing the oxalate and acetate of silver. The experiments of this chemist appear to be executed with a degree of exactness which can scarcely be exceeded, and lead to conclusions of the highest interest, as they give numbers which approach so closely to multiples of 6.25, the half equivalent of hydrogen, that the differences may be safely considered as falling within the unavoidable errors of observation, and the multiple numbers assumed as the true numbers for the three equivalents in question, (Annales, &c. 1846, 3 sér. xviii. 41). The results are:—

	Maumené.	Multiple Numbers.
Chlorine	443.669	443.75 = 6.25 × 71
Potassium	487.004	487.50 = “ × 78
Silver	1350.322	1350.00 = “ × 216

The following short table contains numbers lately obtained by M. Pelouze, for several elements, differing sensibly from the numbers of Berzelius, for which they are substituted, and multiples of 6.25, to which they all closely approximate.

	Berzelius.	Pelouze.	Multiples of 6.25.
Sodium	290.90	287.17	287.50 = 6.25 × 46
Barium	856.88	858.03	856.25 = " × 137
Strontium	547.29	548.02	550.00 = " × 88
Silicium	277.29	266.82	268.75 = " × 43
Phosphorus	392.29	400.30	400.00 = " × 64
Arsenic	940.08	937.50	937.50 = " × 150

The equivalent of sodium was determined from the quantity of chloride of sodium required to precipitate 200 parts of silver from the nitrate. Barium, strontium, silicium, phosphorus, and arsenic, in a similar manner, also by the quantity of silver which their chlorides precipitated.

The equivalent of calcium is taken at 250, after Dumas; MM. Erdmann and Marchand have confirmed this equivalent; Berzelius himself reduces his first number from 256.02 to 251.94. Sulphur and mercury are also after Erdmann and Marchand: Berzelius has, on recalculating his old results, reduced the number for sulphur from 201.17 to 200.8.

The equivalent of iron was lately found 349.80 by MM. Swanberg and Norlin, and their results confirmed by Berzelius, who now obtains 350.27 and 350.369 (instead of 339.21, the old equivalent): an intermediate number 350 is adopted in the table.

The number for zinc is that of M. Axel Erdmann, who took unusual pains in purifying the metal: it is 412.63 according to M. Favre, and 414 according to M. Jacquelain; the number of Berzelius is 403.23.

The number for uranium is that adopted by M. Peligot; it has been found 746.36 by M. Wertheim, and 742.875 by Ebelmen.

The number for gold is that lately deduced by Berzelius from an analysis of the double chloride of gold and potassium (Poggendorff's Annalen, lxv. 314); it replaces his former number 1243.01. Those of cerium and ruthenium are by Hermann (Annuaire de Chimie, 1835, p. 130). M. Rammelsberg has adopted for the former metal 574.7, and M. Beringer 577; the number of M. Hermann is intermediate. Ruthenium, the new metal from native platinum, is considered by its discoverer, Prof. Haus, to be isomorphous with, and to have the same equivalent as, rhodium, from the composition of the double sesqui-chloride of ruthenium and potassium, $2\ K\ Cl + Ru_2Cl_3$.

No data exist for fixing the equivalents of the metallic elements lately discovered, whose names appear in the table, namely, didymium found with lanthanum in cerite (Mosander); niobium and pelopium in the tantalite of Bavaria (H. Rose).

Names of Elements.	Symbols.	Equivalents.		
		Hydrogen =1.	Oxy.=100. H.=12·5.	
Aridium	Ar			
Donarium	Do	79.72	997.4	Do_2O_3, sesquioxide of donarium.
Erbium	E			
Ilmenium	Il	60.4	753.	IlO_2, ilmenic acid.
Norium	No			
Terbium	Tb			

[The elements given in the above table have been made known since the publication of this part of the original work. Aridium by Ulgren, Donarium by Bergemann, Erbium and Terbium by Mosander, Ilmenium by Hermann, and Norium by Svanberg. The equivalents, as far as ascertained, are given on the authority of the discoverers. — R. B.]

In the class of simple substances are placed all those bodies which are not known to be compound, on the principle that whatever cannot be decomposed or resolved by any process of chemistry into other kinds of matter, is to be considered as simple. They are the only bodies the names of which are at present independent of any rule. An attempt was, indeed, made on the first introduction of a systematic nomenclature, to make the names of several of them significant; but some confusion in regard to their derivatives was found to be the consequence of this, and many of them being familiar substances, were almost of necessity allowed to retain the names they bear in common language: such as, sulphur, tin, silver, and the other metals known in the arts. To newly discovered elements, however, such names were applied as were suggested by any striking physical property they possessed, or remarkable circumstance in their history. The names of the newer metals, platinum, potassium, vanadium, &c., have a common termination, which serves to distinguish them as metals. Another class of elementary bodies, resembling each other in certain particulars, is marked in a similar manner; namely, that composed of chlorine, iodine, bromine, and fluorine.

The names of *compound bodies* are contrived to express their composition, and the class to which they belong, and are founded on a distribution of compounds into three orders, namely, first, compounds of one element with another element; as, for instance, oxygen with sulphur in sulphuric acid, or oxygen with sodium in soda, which are called binary compounds. Secondly, combinations of binary compounds with each other, as of sulphuric acid with soda in Glauber's salt, and the salts generally, which are termed ternary compounds. And thirdly, combinations of salts with one another, or double salts, such as alum, which are quaternary compounds.

1.—Of the compounds of the first order, the greater number known to the original framers of the chemical nomenclature contained oxygen as one of their two constituents; and hence an exclusive importance was attached to that element. Its compounds with the other elementary bodies may be divided by their properties into: (*a*) the class of neutral bodies and bases; and (*b*) the class of acids.

(*a*). To members of the first class the generic term *oxide* was applied, the first syllable of oxygen, with a termination (*ide*) indicative of combination; to which the name of the other element was joined to express the specific compound. Thus a compound of oxygen and hydrogen is *oxide of hydrogen;* of oxygen and potassium, *oxide of potassium;* of which compounds, the first, or water, is an instance of a neutral oxide; and the second, or potash, of a base or alkaline oxide. But the same elementary body often combines with oxygen in more than one proportion, forming two or more oxides; to distinguish which the Greek prefix (*proto*, πρῶτος, first) is applied to the oxide containing the least proportion of oxygen; *deuto* (δεύτερος, second) to the oxide containing more oxygen than the protoxide; and trito (τριτος, third) to the oxide containing still more oxygen than the deutoxide; which last oxide, if it contains the largest proportion of oxygen with which the element can unite to form an oxide, is more commonly named the *peroxide;* from *per*, the Latin particle of intensity. Thus, the three compounds of the metal manganese and oxygen are distinguished as follows:—

Names.	Composition. Manganese.	Oxygen.
Protoxide of manganese	100	28.91
Deutoxide of manganese	100	43.36
Peroxide of manganese	100	57.82

As the prefix *per* implies simply the highest degree of oxidation, it may be applied to the second oxide where there are only two, as in the oxides of iron, the second oxide of which is called, indifferently, the deutoxide or peroxide of iron. M. Thenard, in his Traité de Chimie, avoids the use of the term deutoxide, and confines the application of peroxide to such of these oxides as, like the peroxide of manganese, do not combine with acids. He applies the names *sesquioxide* and *binoxide* to oxides, which are capable of combining with acids, and contain respectively, once and a half and twice as much oxygen as the protoxides of the same metal. He has thus the protoxide, sesquioxide, and peroxide of manganese, the protoxide and sesquioxide of iron, the protoxide and binoxide of tin, &c. This distinction is useful, and will be adopted in the present work. Certain inferior oxides, which do not combine with acids, are called *suboxides;* such as the suboxide of lead, which contains less oxygen than the oxide distinguished as the protoxide of the same metal.

The compounds of chlorine and several other elements are distinguished in the same manner as the oxides. Such elements resemble oxygen in several respects, particularly in the manner in which their compounds are decomposed by electricity.

Chlorine, for example, like oxygen, proceeds to the positive pole, and is therefore classed with oxygen as an electro-negative substance, in a division of elements grounded on their electrical relations. Thus, with the other elementary bodies,

Oxygen	forms	oxides,
Chlorine	"	chlorides,
Bromine	"	bromides,
Iodine	"	iodides,
Fluorine	"	fluorides,
Sulphur	"	sulphides (or sulphurets),
Phosphorus	"	phosphides (or phosphurets),
Carbon	"	carbides (or carburets),
Nitrogen	"	nitrides,
Hydrogen	"	hydrides,
Cyanogen ($N C_2$)	"	cyanides,
Sulphion ($S O_4$)	"	sulphionides.

As cyanogen and sulphion, although compound bodies, comport themselves in their combinations like electro-negative elements, their compounds are named in the same manner as the oxides.

When several chlorides of the same metal exist, they are distinguished by the same numerical prefixes as the oxides. Thus we have the protochloride and the sesquichloride of iron; the protochloride, and the bichloride of tin. The compounds of sulphur greatly resemble the oxides, but they have been generally named sulphurets, and not sulphides or sulphurides. Berzelius, indeed, applies the term sulphuret to such binary compounds of sulphur only as are basic and correspond with basic oxides; while sulphide is applied by him to such as are acid, or correspond with acid oxides. Hence, he has the *sulphuret of potassium*, and the *sulphide of arsenic* and *sulphide of carbon*. Compounds of chlorine are distinguished by him into chlorurets and chlorides, on the same principle; thus he speaks of the *chloruret of potassium*, and of the *chloride of phosphorus*. But these distinctions have not served any important purpose, while besides conducing to perspicuity it is an object of some consequence in a systematic point of view to allow the termination *ide*, already restricted to electro-negative substances, to apply to all of them without exception.

The combinations of metallic elements among themselves are distinguished by the general term *alloys*, and those of mercury as *amalgams*.

(*b*). The binary compounds of oxygen which possess acid properties are named on a different principle. Thus the acid compound of titanium and oxygen is called *titanic acid;* of chromium and oxygen, *chromic acid;* or the name of the acid is derived from that of the substance in combination with oxygen, with the termination *ic*. Where the same element was known to form two acid compounds with oxygen, the termination *ous* was applied to that which contained the least proportion of oxygen, as in *sulphurous* and sulphuric acids. On the discovery of an acid compound of sulphur which contained less oxygen than that already named sulphurous acid, it was called *hyposulphurous acid*, (from the Greek ὑπο, under); and another new compound, intermediate between the sulphurous and sulphuric acids, was named *hyposulphuric acid*. On the same principle, an acid containing a greater proportion of oxygen than that already named chloric acid, was named *hyperchloric acid*, (from the Greek ὑπερ, over;) but now more generally *perchloric acid*. The names of the different acid compounds of oxygen and sulphur, which have been referred to for illustration, with the relative proportions of oxygen which they contain, are as follows:

	Composition.	
Names.	Sulphur.	Oxygen.
Hyposulphurous acid	100	50
Sulphurous acid	100	100
Hyposulphuric acid	100	125
Sulphuric acid	100	150

The same system is adopted for all analogous acids. An acid of chlorine, containing more oxygen than chloric acid, is named perchloric acid, and other similar compounds, which all contain an unusually large proportion of oxygen, are distinguished in the same manner; as periodic acid, and permanganic acid. The perchloric acid is also sometimes called *oxichloric;* but this last term does not seem so suitable as the first.

Another class of acids exists in which sulphur is united with the other element in the place of oxygen. The acids thus formed are called *sulphur acids.* The names of the corresponding oxygen acids are sometimes applied to these, with the prefix *sulph,* as *sulpharsenious* and *sulpharsenic* acids, which resemble arsenious and arsenic acids respectively in composition, but contain sulphur instead of oxygen.

Lastly, certain substances, such as chlorine, sulphur and cyanogen, form acids with hydrogen, which are called hydrogen acids, or *hydracids.* In these acid compounds the names of both constituents appear, as in the terms *hydrochloric acid, hydrosulphuric acid,* and *hydrocyanic acid.* Thenard has proposed to alter these names to *chlorhydric, sulphohydric,* and *cyanhydric acids,* which in some respects are preferable terms.

2.—Compounds of the second order, or salts, are named according to the acid they contain, the termination *ic* of the acid being changed into *ate,* and *ous* into *ite.* Thus a salt of sulphuric acid is a *sulphate;* of sulphurous acid, a *sulphite;* of hyposulphurous acid, a *hyposulphite;* of hyposulphuric acid, a *hyposulphate;* and of perchloric acid, a *perchlorate;* and the name of the oxide indicates the species—as sulphate of oxide of silver, or sulphate of silver; for the oxide of the metal being always understood, it is unnecessary to express it, unless when more than one oxide of the same metal combines with acids, as sulphate of protoxide of iron, and sulphate of sesquioxide of iron. These salts are often called protosulphate and persulphate of iron, where the prefixes proto and per refer to the degree of oxidation of the iron. The two oxides of iron are named *ferrous oxide* and *ferric oxide* by Berzelius, and the salts referred to, the ferrous sulphate, and the ferric sulphate. The names stannous sulphate and stannic sulphate express in the same way the sulphate of the protoxide of tin, and the sulphate of the peroxide of tin. But such names, although truly systematic, and replacing very cumbrous expressions, involve too great a change in chemical nomenclature to be speedily adopted. Having found its way into common language, chemical nomenclature can no longer be altered materially without great inconvenience. It must be learned as a language, and not be viewed and treated as the expression of a system. A *super*-sulphate contains a greater proportion of acid than the sulphate or neutral sulphate; a *bi*-sulphate twice as much, and a *sesqui*-sulphate once and a half as much as the neutral sulphate; while a *sub*-sulphate contains a less proportion than the neutral salt; the prefixes referring in all cases to the proportion of acid in the salt, or to the *electro-negative* ingredient, as with oxides. The excess of base in sub-salts is sometimes indicated by Greek prefixes expressive of quantity, as *di*-chromate of lead, *tris*-acetate of lead; but this deviation is apt to lead to confusion. If a precise expression for such subsalts were required, it would be better to say, the bibasic subchromate of lead, the tribasic subacetate of lead. But the names of both acid and basic salts are less in accordance with correct views of their constitution, than the names of any other class of compounds.

Combinations of water with other oxides are called *hydrates:* as hydrate of potassa, hydrate of boracic acid.

3.—In the names of quarternary compounds or of double salts, the names of the constituent salts are expressed, thus:—*Sulphate of alumina and potash* is the compound of sulphate of alumina and sulphate of potash; the name of the acid being expressed only once, as it is the same in both of the constituent salts. The name alum, which has been assigned by common usage to the same double salt, is likewise received in scientific language. The *chloride of platinum and potassium* expresses, in the same way, a compound of chloride of platinum and chloride of potassium. An oxichloride, such as the *oxichloride of mercury,* is a compound of the oxide with the chloride of the same metal.

The first ideas of a chemical nomenclature are due to Guyton de Morveau, whose views were published in 1782; but the chief merit of the construction of the valuable system in use is justly assigned to Lavoisier, who reported to the French Academy on the subject, in the name of a committee, in 1787. It has not been materially modified or expanded since its first publication. The present, or Lavoisierian nomenclature, does not furnish precise expressions for many new classes of compounds, the existence of which was not contemplated by its inventors, and many of its names express theoretical views of the constitution of bodies which are doubtful, and not admitted by all chemists. But its deficiencies are supplied, and the composition of bodies more accurately represented, in certain written expressions, or chemical formulæ, which are also employed to denote particular substances, and which form a valuable supplement to the nomenclature still generally used. These formulæ are constructed on the simplest principles, and besides supplying the deficiencies of the nomenclature, they at once exhibit to the eye the composition of bodies, and afford a mechanical aid in observing relations in composition, of the same kind as the use of figures in the comparison of arithmetical sums.

Symbols of the elements.—Each elementary substance is represented by the initial letter of its Latin name, as will be seen by reference to the table of elementary substances, page 102; but when the names of two or more elements begin with the same letter, a second in a smaller character is added for distinction; thus oxygen is represented by the letter O, the metal osmium by Os, fluorine by F, and iron (ferrum) by Fe; small letters, it is to be observed, never being significant of themselves, but employed only in connexion with the large letters as distinctive adjuncts. These symbols represent, at the same time, certain relative quantities of the elements, the letter O expressing not oxygen indefinitely, but 100 parts by weight of oxygen, and Fe 350 parts by weight of iron, or any other quantities of these two substances which are in the proportion of these numbers: 8 parts of oxygen, for instance, and 28 of iron. It will immediately be explained that the elementary bodies combine with each other in certain proportional quantities only, which are expressed by one or other indifferently of the two series of numbers placed against the names of the elements in the table referred to. These quantities are conveniently spoken of as the combining proportions, the equivalent quantities, or *the equivalents* of the elements. The symbol, or letter, of itself representing *one* equivalent of the element, several equivalents are represented by repeating the symbol, or by placing figures before it; thus Fe Fe, or 2 Fe, and 3 O, mean two equivalents of iron and three of oxygen. Or small figures are placed either above or below the symbol, and to the right; thus Fe^2, and O^3, or $Fe_2\,O_3$, are of the same value as the former expressions, but are used only when symbols are placed together in the formulæ of compounds. Two equivalents of an element are sometimes expressed by placing a dash through, or under its symbol, but such abbreviations will not be made use of in the present work.

Formulæ of compounds.—The collocation of symbols expresses combination: thus Fe O represents a compound of one equivalent or proportion of iron, and one of oxygen, or the protoxide of iron; SO_3, a compound of one equivalent of sulphur, and three of oxygen—that is, one equivalent of sulphuric acid; and sulphate of iron itself, consisting of one equivalent of each of the preceding compounds, may be represented as follows:

$$Fe\,O \quad S\,O_3, \text{ or}$$
$$Fe\,O + S\,O_3, \text{ or}$$
$$Fe\,O, \quad S\,O_3.$$

The sign plus (+) or the comma, being introduced in the second and third formulæ, to indicate a distribution of the elements of the salt into its two proximate constituents, oxide of iron, and sulphuric acid, which is not so distinctly indicated in the first formula. It may often be advantageous to make use of both the comma and the plus sign in the same formula, and then it would be a beneficial practice to use them as in the following formula for the double sulphate of iron and potash:

$$\mathrm{Fe\,O,\ SO_3 + KO,\ SO_3},$$

in which the comma is employed to indicate combination more intimate in degree, or of a higher order than the plus sign, namely, of the oxide with the acid in each salt, while the combination of the two salts themselves is expressed by the sign $+$.

The small figures in the preceding formulæ affect only the symbol or letter to which they are immediately attached. Larger figures placed before and in the same line with the symbols apply to the *compound* expressed by the symbols. Thus $3\ \mathrm{S\,O_3}$, means three equivalents of sulphuric acid; $2\ \mathrm{Pb\,O}$, two equivalents of oxide of lead. But the interposition of the comma or plus sign prevents the influence of the figure extending farther, thus

$$2\ \mathrm{Pb\,O,\quad Cr\,O_3},\ \text{or}$$
$$2\ \mathrm{Pb\,O + Cr\,O_3},$$

is two proportions of oxide of lead, and one of chromic acid, or the sub-chromate of lead. To make the figure apply to symbols which are separated by the comma or plus sign, it is necessary to enclose all that is to be affected within brackets, and place the figure before them. Thus,

$$2\ (\mathrm{Pb\,O,\ Cr\,O_3})$$

means two proportions of neutral chromate of lead. The following formulæ of two double salts with their water of crystallization, exhibit the application of these rules:—

Iron-alum, or the sulphate of peroxide of iron and potash:

$$\mathrm{KO,\ SO_3 + Fe_2\,O_3,\ 3\ SO_3 + 24\ HO}$$

Oxalate of peroxide of iron and potash:

$$3\ (\mathrm{K\,O,\ C_2\,O_3}) + \mathrm{Fe_2\,O_3,\ 3\ C_2\,O_3 + 6\ HO}.$$

It will be found to conduce to perspicuity, to avoid either connecting two formulæ of different substances not in combination, by the sign plus, or allowing them to be separated merely by a comma, as the plus and comma *between* symbols or formulæ are conventionally understood to unite the formulæ into one, and to express combination; and indeed it is advisable to write every complete formula apart, and in a line by itself, if possible.

The only other circumstance to be attended to in the construction of such formulæ is the *arrangement* of the symbols or letters, which is not arbitrary. In naming a binary compound, such as oxide of iron, chloride of potassium, &c., we announce first the oxygen or element most resembling it in the compound; that is, the electro-negative ingredient; but in the formulæ of the same bodies, it is the other or the electro-positive element which is placed first, as in $\mathrm{Fe\,O}$, and $\mathrm{K\,Cl}$. In the formulæ of salts, it is likewise the basic oxide or electro-positive constituent which is placed first, and not the acid. Thus the sulphate of potash is $\mathrm{K\,O,\ S\,O_3}$, and not $\mathrm{S\,O_3,\ KO}$. Information respecting the constitution of a compound may often be expressed in its formula, by attending to this rule. Thus sulphuric acid of specific gravity 1.780, contains two proportions of water to one of acid, but by giving to it the following formula:

$$\mathrm{H\,O,\ S\,O_3 + HO},$$

we express that one proportion only of water is combined as a base with the acid, and that the second proportion of water, the formula of which follows that of the acid, is in combination with this sulphate of water.

The above system of notation is complete, and sufficiently convenient for representing all binary compounds, and compounds belonging to the organic department of the science, in the formulæ of which the ultimate elements only are expressed.

But when salts and double salts are expressed, the formulæ sometimes become inconveniently long. They may often be greatly abbreviated, and made more distinct, by expressing each equivalent of oxygen in an oxide or acid, by a point placed over the symbol of the other element, thus:

Protoxide of iron, $\dot{\mathrm{F}}\mathrm{e}$.

Sulphuric acid, $\dddot{\mathrm{S}}$.

Crystallized sulphate of protoxide of iron, $\mathrm{Fe}\,\dddot{\mathrm{S}},\ \dot{\mathrm{H}}+6\dot{\mathrm{H}}$.

Alum, $\dot{\mathrm{K}}\,\dddot{\mathrm{S}},\ \overset{\cdots}{\mathrm{Al\,Al}}\,\dddot{\mathrm{S}}_3+24\dot{\mathrm{H}}$.

Felspar, $\dot{\mathrm{K}}\,\overset{\cdots}{\mathrm{Si}},\ \overset{\cdots}{\mathrm{Al\,Al}}\,\overset{\cdots}{\mathrm{Si}}_3$.

Oxalate of peroxide of iron and potash, $3\dot{\mathrm{K}}\,\overset{\cdots}{\mathrm{CC}}+\overset{\cdots}{\mathrm{Fe\,Fe}},\ 3\overset{\cdots}{\mathrm{CC}}+6\dot{\mathrm{H}}$.

Such formulæ are more compact, and more easily compared with each other, the relation between the mineral felspar and alum without its water of crystallization, being seen at a glance on thus placing their formulæ together; the one having the symbol for silicium, the other that for sulphur, but everything else remaining the same. This abbreviated plan also exhibits more distinctly the relation between the equivalents of oxygen in the different constituents of a salt, which is always important.

It is to be observed, that the oxygen expressed by the points placed over a letter is brought under the influence of the small figure attached to that letter: as, for example, $\dddot{\mathrm{S}}_3$ in the preceding formula of alum, means three equivalents of sulphuric acid; so that this sign has the same value as if it were written 3 $\dddot{\mathrm{S}}$.

Equivalents of *sulphur* are likewise sometimes expressed by commas placed over other symbols, as the trito-sulphuride of arsenic by $\overset{,,,}{\mathrm{As}}$; but such compounds are not of constant occurrence like the oxides, and do not create the same necessity for a new and arbitrary symbol. A compound body, such as cyanogen, which combines with a numerous series of other bodies, is often for brevity expressed by the initial letter or letters of its name, as—

Cyanogen	Cy,
Ethyl	E;

and the organic acids are sometimes expressed by a letter in the same way, but with the minus sign (—) placed over it: thus—

Acetic acid, by $\overline{\mathrm{A}}$,
Tartaric acid, by $\overline{\mathrm{T}}$.

But arbitrary characters of this kind will always be explained on the occasion of their introduction.

SECTION II.—COMBINING PROPORTIONS.

All analyses prove that the composition of bodies is fixed and invariable: 100 parts of water are uniformly composed of 11.1 parts by weight of hydrogen, and 88.9 parts of oxygen, its constituents never varying either in nature or proportion. This and other substances may exist in an impure condition, from an admixture of foreign matter, but their own composition remains the same in all circumstances. It is this constancy in the composition of bodies which gives to chemical analyses all their value, and rewards the vast care necessarily bestowed upon their execution.

An examination of the composition of a class of bodies, such as the oxides, containing an element in common, shows that any one element unites with very different quantities of the other elements. Thus in each of the five oxides of which the composition is given on page 112, the oxygen and other constituents appear in a different relation to each other:

Composition of Oxides.

Water.	Oxide of Copper.	Oxide of Zinc.	Oxide of Lead.	Oxide of Silver.
Oxygen ... 88.9	Oxygen 20.2	Oxygen ... 19.1	Oxygen ... 7.2	Oxygen 6.9
Hydrogen 11.1	Copper 79.8	Zinc 80.9	Lead 92.8	Silver 93.1
100	100	100	100	100

But the relation between the oxygen and the other constituent in these oxides will be seen more distinctly by stating their composition in such a way as to have the oxygen expressed by the same number in every case, or made equal to 100 parts. Thus:

Composition of Oxides.

Water.	Oxide of Copper.	Oxide of Zinc.	Oxide of Lead.	Oxide of Silver.
Oxygen . 100	Oxygen 100	Oxygen ... 100	Oxygen ... 100	Oxygen 100
Hydrogen 12.5	Copper 396	Zinc 406	Lead 1294	Silver 1350
112.5	496	506	1394	1450

From which it follows, that—

12.5 parts of hydrogen,
396 parts of copper,
406 parts of zinc,
1294 parts of lead,
1350 parts of silver,
combine with 100 *parts of oxygen.*

These numbers prove to be in some degree characteristic of the substances to which they are here attached, for when the composition of the *sulphides* of the same substances is examined, it is found that exactly corresponding quantities of hydrogen, copper, &c. likewise combine with one and the same quantity of sulphur, although not with 100 parts of that element as of oxygen. The conclusion from an examination of the sulphides is, that—

12.5 parts of hydrogen,
396 parts of copper,
406 parts of zinc,
1294 parts of lead,
1350 parts of silver,
combine with 200 *parts of sulphur.*

An examination of the *chlorides* of the same five elements likewise proves, that—

12.5 parts of hydrogen,
396 parts of copper,
406 parts of zinc,
1294 parts of lead,
1350 parts of silver,
combine with 443.75 *parts of chlorine.*

Hydrogen, copper, &c., are indeed found to unite in the proportions repeated above, with a certain or constant quantity of all other elements; as, for example, with 978 *bromine*, with 1580 *iodine*, &c.

On extending the inquiry to other substances, it appears that for each of them a number may be found which expresses in like manner the proportion in which that substance unites with 100 parts of oxygen, 200 of sulphur, 443.73 of chlorine, &c. These numbers constitute the combining proportions, or equivalent quantities of bodies, which are introduced in the table of the names of the elements at the beginning of this chapter, and which are the quantities understood to be expressed by the chemical symbols of these bodies.

Any series of numbers may be chosen for the combining proportions, provided the true relation between them is preserved, as in the first series of numbers given in the same table, which are all 12½ times less than the numbers of the second series. Hydrogen is reduced from 12.5 to 1, oxygen from 100 to 8, sulphur from 200 to 16: altered in the same proportion, copper becomes 31.66, zinc 32.52, lead 103.56, and silver 108. This series, or the hydrogen scale, is recommended by the circumstance that its numbers are smaller and more easily recollected than those of the other, or oxygen scale. The equivalents of several of the most important elements are now also generally allowed to be the exact multiples of the equivalent of hydrogen, so that the equivalent of the latter element being 1, the equivalents of the former are accurately expressed by entire numbers;—carbon by 6, oxygen by 8, nitrogen by 14, sulphur by 16, and iron by 28.

Having reference to the oxygen series, it is said, in general terms, that the combining proportion of a simple substance represents the quantity of that substance which combines with 100 parts of oxygen to form a protoxide. On the hydrogen scale, which I shall adopt, the definition of a chemical equivalent, or combining proportion becomes as follows:—*The combining proportion of a simple substance represents the quantity of that substance which unites with* 8 *parts of oxygen to form a protoxide.*

The first law of combination is, that "bodies unite with each other in their combining proportions only, or in multiples of them, and in no intermediate proportions." This law may be illustrated by the compounds of nitrogen and oxygen, which are five in number, and are composed as follows:—

Protoxide of nitrogen	nitrogen 14, oxygen 8.
Deutoxide of nitrogen	nitrogen 14, oxygen 16.
Nitrous acid	nitrogen 14, oxygen 24.
Peroxide of nitrogen	nitrogen 14, oxygen 32.
Nitric acid	nitrogen 14, oxygen 40.

The first compound consists of a single combining proportion of each of its constituents. But in the other compounds, a single proportion of nitrogen is united with quantities of oxygen which correspond exactly with two, three, four, and five combining proportions of that element. In the greater number of binary compounds one of the constituents at least is present in the proportion of a single equivalent, like the nitrogen in this series, while the other constituent, generally the oxygen in oxides, and the electro-negative element in other compounds, is present in a multiple of its combining proportion. But the number of equivalents which may enter into a compound is subject to considerable variation, as will appear from the following examples:—

One	eq. of	oxygen	+	One	eq. of	hydrogen,	forms	water.
Two	"	oxygen	+	One	"	hydrogen,	form	peroxide of hydrogen.
One	"	oxygen	+	Two	"	copper,	forms	suboxide of copper.
One	"	sulphur	+	Three	"	oxygen,	"	sulphuric acid.
Two	"	sulphur	+	Two	"	oxygen,	form	hyposulphurous acid.
Two	"	iron	+	Three	"	oxygen,	"	peroxide of iron.
Two	"	sulphur	+	Five	"	oxygen,	"	hyposulphuric acid.
Two	"	manganese	+	Seven	"	oxygen,	"	hypermanganic acid.

Representing the constituents of a binary compound by A and B, the last being the oxygen or electro-negative constituent, the most frequent combinations are—$A+B$, $A+2B$, $A+3B$, and $A+5B$. The combination of $2A+3B$, is not unfrequent, but $2A+B$, $A+4B$, $A+7B$, $2A+2B$, or $2A+5B$, are of comparatively rare occurrence. Combination between two elements is not known to occur in more complicated ratios than the preceding, if the compounds of carbon and hydrogen be excepted, which are numerous, and exhibit great diversity of composition, like the compounds of organic chemistry generally, to which they properly belong.

Combination likewise takes place among bodies which are themselves compound, in proportional quantities, which are fixed and determined by the law, that "the combining number of a compound body is always the sum of the combining numbers of its constituents." Thus oil of vitriol, which contains water and sulphuric acid, is composed of these bodies in the proportion of—

Water	9
Sulphuric acid	40

in which the combining proportion of the water (9) is the sum of the equivalents of its constituents; namely, of oxygen 8, and of hydrogen 1; and that of sulphuric acid (40), of those of sulphur 16, and of oxygen 24; there being three proportions of oxygen in sulphuric acid. The combining proportion of oxide of zinc is 40.52, the sum of oxygen 8, and zinc 32.52; and the compound of this oxide with sulphuric acid, or the salt, sulphate of zinc, consists of—

Oxide of zinc	40.52
Sulphuric acid	40.
	80.52

Of potash, the combining proportion is 47; or oxygen 8, added to potassium 39; and to this proportion of potash the usual proportion of sulphuric acid is attached in the sulphate of potash, which is composed of—

Potash	47
Sulphuric acid	40
	87

Of these salts themselves, the combining proportions ought to be the sums obtained by the addition of the numbers of their constituents; and accordingly the double sulphate of zinc and potash consists of—

Sulphate of zinc	80.52
Sulphate of potash	87
	167.52

Of nitric acid the constituents are one eq. of nitrogen 14, and five of oxygen 40, making together 54, which is the combining proportion of that acid, and is found to unite with 9 water, with 40.52 oxide of zinc, and with 47 potash; or with the same quantities of these oxides as combine with 40 sulphuric acid. Carbonic acid is composed of one proportion of carbon 6, and two proportions of oxygen 16, so that its combining number is 22; in which proportion it unites with 47 potash, to form carbonate of potash. The equivalent quantities of all other acids and bases correspond in like manner with the numbers deducible from their composition. Indeed, the law is found to hold in compounds of every class and character, and whether they contain few or many equivalents of their elements.

Compound bodies likewise unite among themselves in multiples of their combining proportions, as well as in single equivalents. Thus 47 potash combine with 52.15 chromic acid, and with double that quantity, or 104.30, chromic acid, to form the yellow and red chromates of potash; the first containing one equivalent, and the second two equivalents of acid. The occurrence of multiple proportions was well illustrated by Dr. Wollaston in the carbonate and bicarbonate of potash. A quantity of the latter salt being divided into equal parts, one-half was exposed to a red heat, by the effect of which the salt lost some carbonic acid and became neutral carbonate; and both portions being afterwards decomposed by an acid, the salt in its original condition was found to afford a measure of carbonic acid gas exactly double of that yielded by the portion exposed to the high temperature. By experiments equally simple and convincing, he proved that in the three salts formed by oxalic acid and potash, the quantities of acid which combine with the same quantity of alkali are rigorously among themselves as the numbers 1, 2, and 4. The composition of all other super and sub-salts is found to be in conformity with the same law, one of the constituents being always present in the proportion of two or more equivalents.

The combining proportions of compound bodies depend entirely, therefore, upon those of their constituents, or upon the equivalents of the elementary bodies. The mode of determining these fundamental equivalents generally consists, as may be anticipated, in ascertaining the quantity of any element which exists united with 8 parts of oxygen in the protoxide of that element, which quantity is viewed as a single equivalent. Thus, of hydrogen and lead, the protoxides are water and litharge, in which respectively 8 oxygen are associated with 1 hydrogen and 103.56 lead, which numbers are therefore single equivalents of these elementary substances. But the difficulty still remains to know what is a protoxide; for the rule is not followed in all cases to consider that oxide of an element as the protoxide which contains the least proportion of oxygen. When only one oxide is known, it is presumed to be a protoxide, and composed of single equivalents, unless it corresponds in properties with a higher degree of oxidation of some other element; and of several oxides of the same element, that containing least oxygen is viewed as the protoxide, unless a higher oxide has better claims to be considered as such. Hence magnesia and oxide of zinc being the only oxides of magnesium and zinc known, are protoxides; and water, litharge, potash, soda, lime, and protoxide of iron, which are all the lowest oxides of different metals, are admitted without objection to be protoxides, and become standards of comparison for this class of bodies; while alumina, the only oxide of aluminum, differing entirely from the protoxide of iron, but closely resembling the peroxide of that metal, is considered a peroxide of similar constitution, or to contain three equivalents of oxygen and two of metal. Now in alumina 24 oxygen, or three equivalents, are united with 27.38 aluminum, one-half of which number, or 13.69, is therefore the equivalent of aluminum. The true protoxide of aluminum, if it is capable of existing, still remains to be discovered. The green oxide of chromium, which was till lately the lowest degree of oxidation known of that metal, was notwithstanding considered a peroxide, being analogous to alumina and the peroxide of iron. On the other hand, the second degree of the oxidation of copper, or the black oxide, and not the first degree of oxidation of that metal, must be viewed as the protoxide, or as composed of single equivalents, from its correspondence with the protoxide of iron and a large class of admitted protoxides. The lower degree of oxidation of copper or the red oxide, which contains only half the proportion of oxygen in the black oxide, comes therefore to be considered a suboxide; a compound of two equivalents of metal and one of oxygen. For reasons somewhat similar, the higher of the two grades of oxidation of mercury, or the red oxide of that metal, is now generally received as the protoxide, and the ash-coloured oxide reputed a suboxide. These suboxides of mercury and copper are capable of combining with acids, but they are the only suboxides which possess that property. It is the character of metallic protoxides to form salts with acids; and of several oxides of the same metal, the protoxide is always the most powerful base.

Bodies likewise *replace* each other in combination, in equivalent quantities. Thus in the decomposition of water by chlorine, which occurs in certain circumstances, 35.5 parts of chlorine unite with 1 hydrogen or one equivalent of that body, to form hydrochloric acid, and displace at the same time and liberate 8 parts of oxygen. Hence the number 35.5 represents the combining proportion of chlorine, which is equivalent in combination to, or can be substituted for, 8 oxygen. Again, in decomposing hydriodic acid, 35.5 chlorine unite with 1 hydrogen, and liberate 126.36 iodine, which proportion of iodine may again acquire 1 hydrogen, by decomposing sulphuretted hydrogen, and set free 16 sulphur. Hence 126.36 and 16 are the equivalent quantities of iodine and sulphur, which take the place of 35.5 chlorine or 8 oxygen in combination with 1 hydrogen.

When 32.52 grains of zinc are introduced into a solution of nitrate of copper, they dissolve, acquiring 8 oxygen and 54 nitric acid, and become nitrate of zinc, while 31.66 parts of metallic copper are deposited, which had previously been in the state of nitrate, and in combination with the above-mentioned quantities of oxygen and nitric acid, and the solution remains otherwise unaltered. Zinc throws down nearly all the metals from their solutions in acids in the same manner, and if the quantity of this substance introduced into the solutions, and dissolved, be a combining proportion, as in the instance given, the quantities of the metals precipitated will also be combining proportions of those metals. The quantity of zinc employed may be varied, but the quantity of other metal precipitated will still be, to the quantity of zinc dissolved, in the ratio of the combining numbers of the two metals. Lead, copper, tin, or any other metal, when it acts like zinc as a precipitant, likewise throws down equivalent quantities of other metals, and takes their place in the pre-existing compound. This substitution of one metal for another, in a saline compound, without any change in the character of the compound, shows how justly the combining proportions of bodies are termed their equivalent quantities or equivalents. The metal displaced, and that substituted for it, have evidently the same value in the construction of the compound, and are truly equivalent to each other.

The equivalent proportions of such oxides as are bases are ascertained by finding what quantity of each saturates the known combining proportion of an acid. Thus, to saturate 40 parts, or a combining proportion of sulphuric acid, the following proportions of different bases are requisite, and are equivalent in producing that effect:

Magnesia	20.67
Lime	28
Soda	31
Protoxide of manganese	35.67
Potassa	47
Strontia	51.84
Baryta	76.64
Protoxide of lead	111.56
Oxide of silver	116

The addition of these bodies to sulphuric acid in the above proportions destroys its sour taste and other properties as an acid, of which one of the most characteristic is that of reddening certain vegetable blue colours, such as litmus. The acid is said to be neutralized or saturated, and the product or compound formed is a neutral salt, which does not alter the blue colour of litmus. Of the bases mentioned, magnesia has the greatest saturating power, and oxide of silver the least; the proportion of these bases necessary to saturate the same quantity of sulphuric acid being 20.67 of the former, and 116 of the latter.

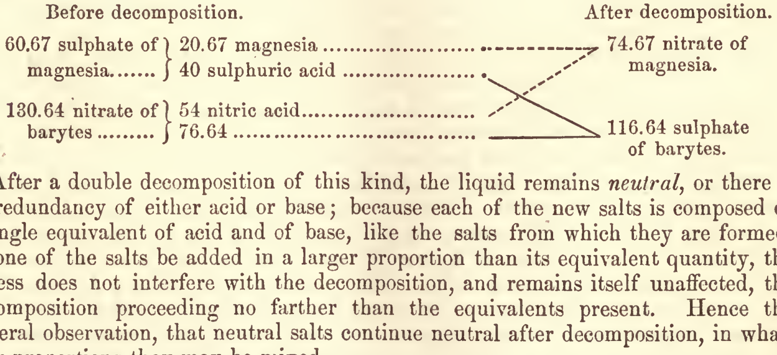
Conversely, the equivalent proportions of acids are the quantities which neutralize the known equivalent of any base or alkali. Thus 47 parts of potassa, or a combining proportion, is deprived of its alkaline properties,—of which the most obvious are its caustic taste and power to restore the blue colour of reddened litmus,—by the following proportions of different acids, and a neutral compound or salt produced in every case:—

Sulphurous acid	32
Sulphuric acid	40
Hydrochloric acid	36.5
Nitric acid	54
Chloric acid	75.5
Hyperchloric acid	91.5
Iodic acid	166.36
Hyperiodic acid	182.36

It thus appears that the acids differ as widely among themselves in their equivalent quantities as the bases do. The equivalent of either an acid or base thus deduced from its neutralizing power is always the same as that indicated by its composition, namely the sum of the equivalent numbers of its constituents. As the bases which saturate acids fully are all protoxides, it also necessarily follows that 100 parts of oxygen are always contained in the proportion of base which neutralizes the equivalent of an acid.

The equivalents of both acids and bases are likewise observed in those decompositions in which one acid is substituted for another acid in combination, or one base for another base. Thus an equivalent of sulphuric acid is found to disengage the equivalent quantity exactly of sulphurous acid from the sulphite of soda, of nitric acid from the nitrate of potash, or of hydrochloric acid from the chloride of sodium, and to replace it in combination with the base, forming in every case a neutral sulphate. An equivalent of potash separates in like manner an equivalent of magnesia, of lime, of barytes, or of protoxide of lead, from its combination with an acid. The proportion of acid or base necessary to produce a certain amount of decomposition may therefore be calculated from a knowledge of the equivalents of bodies; and such knowledge comes to be of the most frequent and valuable application for practical purposes.

But the substitution of equivalent quantities of different bodies for one another is most strikingly exhibited in the decompositions which follow the mixture of certain neutral salts. An equivalent of sulphate of magnesia being mixed with an equivalent of nitrate of barytes, the two bases exchange acids, the original salts disappear completely, and two new salts are produced—the sulphate of barytes, which is insoluble and precipitates, and the nitrate of magnesia, which remains in solution; as represented in the following diagram, in which the equivalent quantities are expressed:—



Before decomposition. After decomposition.

60.67 sulphate of magnesia { 20.67 magnesia; 40 sulphuric acid

130.64 nitrate of barytes { 54 nitric acid; 76.64

74.67 nitrate of magnesia.

116.64 sulphate of barytes.

After a double decomposition of this kind, the liquid remains *neutral*, or there is no redundancy of either acid or base; because each of the new salts is composed of a single equivalent of acid and of base, like the salts from which they are formed. If one of the salts be added in a larger proportion than its equivalent quantity, the excess does not interfere with the decomposition, and remains itself unaffected, the decomposition proceeding no farther than the equivalents present. Hence the general observation, that neutral salts continue neutral after decomposition, in whatever proportions they may be mixed.

But the modes of fixing the equivalent numbers which have been stated are inapplicable to several elementary bodies; such as nitrogen, phosphorus, carbon, boron, and some metals of which the protoxides are not bases, and are uncertain. Nitrogen enters into nitric acid, of which acid it is known that the equivalent is 54, and that it contains five equivalents or 40 parts of oxygen, and consequently 14 parts of nitrogen. It is doubtful, however, whether 14 represents one or two equivalents of nitrogen. But the equivalent of ammonia likewise contains 14 nitrogen, and a less proportion is never found in the equivalent of any other compound into which that element enters. The number 14 is, therefore, *the least combining proportion* of nitrogen, and must on that account be taken as one equivalent. The equivalent of phosphorus can be shown on the same principle to be 32, that of arsenic 75, and that of antimony 129, as given in the tables, and not the halves of these numbers, as often estimated. These three bodies agree with nitrogen in their chemical relations, and the numbers recommended represent the quantities which replace 14 of nitrogen in analogous compounds. The equivalent of carbon may be deduced from the known equivalent of its compound, carbonic acid: but the equivalents of boron and silicium cannot be fixed upon with the same certainty, owing to the doubt which hangs over the equivalents of boracic and silicic acids.

Of the facts which involve the principle of combination in definite and equivalent proportions, the last mentioned appears to have been the first observed and explained. Wenzel, of Freiberg in Saxony, so far back as 1777, made an analysis of a great variety of salts with surprising accuracy, which enabled him to perceive that the neutrality which is observed after the reciprocal decomposition of neutral salts depends upon this,—that the quantities of different acids which saturate an equal weight of one base will also saturate equal weights of any other base.

Richter of Berlin confirmed and extended the observations of Wenzel, attaching proportional numbers to the acids and bases, and remarking for the first time that the neutrality does not change during the precipitation of metals by each other, and also that the proportion of oxygen in the equivalents of bases is the same in all, and may be represented by 100 parts. But the first foundations of a complete system of equivalents, embracing both simple bodies and their compounds, were laid by Dalton, at the same time that he announced his atomic theory. (New System of Chemical Philosophy, 1807). The observation that the equivalent of a compound body is the sum of the equivalents of its constituents, and the discovery of combination in multiple proportions, are peculiarly his. Dr. Wollaston afterwards adapted the more important equivalents to the common sliding rule of Gunter, by means of which, proportions can be observed without the trouble of calculation. This instrument, which is known under the name of *the scale of chemical equivalents*, contributed largely to the diffusion of the knowledge of the proportional numbers, but is not itself of much practical value.

The numerical accuracy of the equivalents assigned to bodies depends entirely upon the exactness of the chemical analyses from which they are deduced. The generally received series of numbers, which is adopted in this work, was drawn up by Berzelius from data supplied in a great measure by himself. The consideration of the laws of Wenzel and Richter, which were long overlooked or misunderstood, was revived by him, and by a series of analytical researches unrivalled for their extent and accuracy he first impressed upon chemistry the character of a science of number and quantity, which is now its highest recommendation. Several of Berzelius's numbers received a valuable confirmation from Dr. Turner, whose inquiries were especially directed to test an hypothesis respecting them proposed and ably maintained by Dr. Prout; namely, that the equivalents of all the elements are multiplies of the equivalent of hydrogen, and consequently if that equivalent be made equal to 1, all the others will be whole numbers. (Phil. Trans. 1833, p. 523). Dr. Penny took a part in the same inquiry, (Ibid. 1839, p. 13). More lately laborious researches have been undertaken with the same object by Dumas, Marignac, Pelouze, and others, whose results are quoted under the table of equivalents. It appears to be definitively settled that the equivalents of the elements are not, without exception, multiples of the equivalent of hydrogen. The number for chlorine (35·5) is conclusive against that hypothesis. At the same time, the accurate determinations of the equivalents of chlorine, silver, and potassium, by Maumené, lend positive support to the opinion that these and all other equivalents are multiples of half the equivalent of hydrogen. So do the recent determinations of carbon and hydrogen in reference to oxygen, and those of nitrogen, sodium, iron, and calcium. The number for lead also, upon the determination of which extraordinary pains have been bestowed by Berzelius at different times, namely 103·56, is favourable to the same view. Now these are the equivalents upon which, above all others, our knowledge is most precise and certain.

Might not, therefore, the equivalent of hydrogen be divided by two, by which chlorine would become 71 and lead 207, hydrogen being 1? The multiple relation would not, however, be established by dividing the equivalent of hydrogen, for, as is justly observed by Berzelius, the chemical reasons which are adduced for the division of the equivalent of hydrogen apply with equal force to the equivalent of chlorine, and the one cannot be divided without dividing the other. The equivalent of chlorine would, therefore, still remain a multiple of half the equivalent of hydrogen.

SECTION III.—ATOMIC THEORY.

The laws of combination, and the doctrine of equivalents, which have just been considered, are founded upon experimental evidence only, and involve no hypothesis. The most general of these laws were not however suggested by observation, but by a theory of the atomic constitution of bodies, in which they are included, and which affords a luminous explanation of them. The partial verification which this theory has received in the establishment of these laws adds greatly to its interest, and is a strong argument in favour of its truth. It is the atomic theory of Dalton, the essential part of which may be stated in a few words.

Although matter appears to be divided and comminuted in many circumstances to an extent beyond our powers of conception, it is possible that it may not be indefinitely divisible; that there may be a limit to the successive division or secability of its parts; a limit which it may be difficult or impossible to reach by experiment, but which nevertheless exists. Matter may be composed of ultimate particles or atoms, which are not farther divisible, and each of which possesses a certain absolute and possibly appreciable weight. Now the question arises, is the atom in every kind of matter of the same weight, or do atoms of different kinds of matter differ in weight? Are the ultimate particles, for instance, to which charcoal and sulphur are reducible, of the same or different weights? Let their weights be supposed to be different, to be in the proportion of the equivalent numbers of sulphur and charcoal, which thus become *atomic weights*, and so of the atoms of other elementary bodies, and the whole laws of combination follow by the simplest reasoning. The atoms of the elementary bodies may be represented to the eye by spheres or by circles in which their symbols are inscribed to distinguish them, as in the following examples, with their relative weights.

Name.	Atom.	Weight of Atom.
Oxygen	Ⓞ	8
Hydrogen	Ⓗ	1
Nitrogen	Ⓝ	14
Carbon	Ⓒ	6
Sulphur	Ⓢ	16
Lead	(Pb)	103.56

Chemical combination takes place between the atoms of bodies, which then come into juxtaposition; and in decomposition the simple atoms separate again from each other, in possession of their original properties. The atom or integrant particle of a compound body is an aggregation of simple atoms, and must therefore have a weight equal to the sum of their weights; as will be obvious from the exhibition of the atomic constitution of a few compounds.

	Atom.	Weight.
Water (oxide of hydrogen)	ⒽⓄ	1 + 8 = 9
Protoxide of nitrogen	ⓃⓄ	14 + 8 = 22
Deutoxide of nitrogen	ⓃⓄⓄ	14 + 16 = 30
Sulphuric acid	ⓈⓄⓄⓄ	16 + 24 = 40
Oxide of lead	(Pb)Ⓞ	103·56 + 8 = 111·56
Sulphate of lead	(Pb)Ⓞ ⓈⓄⓄⓄ	111·56 + 40 = 151·56

It is unnecessary to make any assumption as to the nature, size, form, or even actual weight of the atoms of elementary bodies, or as to the mode in which they are grouped or arranged in compounds. All that is known or likely ever to be known respecting them is their relative weight. The atom of oxygen is eight times heavier than that of hydrogen, but their actual weights are undetermined. To afford the means of expressing the relative weights of these and other atoms, a number which is entirely arbitrary is assigned to one of them, namely 8 to the atom of oxygen, and then the weight of the atom of hydrogen can be said to be 1, of nitrogen 14, of carbon 6, of sulphur 16, and of lead 103·56. A single atom of water contains one atom of oxygen (8), and one of hydrogen (1), and must therefore weigh 9; an atom of oxide of lead contains one atom of oxygen and one of lead, which weigh together 111·56; an atom of sulphuric acid, one atom of sulphur and three atoms of oxygen, which weigh together 40; and an atom of sulphate of lead, including one of each of the preceding compound atoms, must weigh 111·56+40, or 151·56.

The equivalent quantities being now represented by atoms, it necessarily follows that bodies can combine in these quantities or multiples of them only, and not in intermediate proportions, for atoms do not admit of division. In a series of several compounds of the same elements, such as the oxides of nitrogen, which was formerly referred to in illustration of combination in multiple proportions (page 113), one atom of nitrogen combines with one, two, three, four and five atoms of oxygen, and a simple ratio between the quantities of oxygen in these compounds is the consequence. The equivalent of the compound body also is the sum of the equivalents of its constituents, for the weight of a compound atom is the weight of its constituent atoms.

By the juxtaposition, separation, and exchange of one atom for another in compounds, all kinds of combination and decomposition in equivalent quantities may be produced, while the substitution of ponderable masses for the abstract idea of equivalents renders the whole changes most readily conceivable.

This theory being adopted as a useful, while it is at the same time a highly probable representation of the laws of combination, its terms atom or atomic weight may be used as synonymous with equivalent, equivalent quantity, and combining proportion.

M. Dumas is disposed to modify the atomic theory so far as to allow the divisibility of the atoms or ultimate masses in which a body enters into combination, and to suppose that they are groups of more minute atoms, into which they may be divided by physical, but not by chemical forces. He distinguishes the atoms which correspond with equivalents as *chemical atoms*, and allowing them to represent truly and constantly the least quantities in which bodies combine, still supposes that under the influence of heat, and perhaps other physical agencies, these molecules may be subdivided into atoms of an inferior order, of which, for example, two, four, or a thousand, are included in a single chemical atom. (Leçons sur la Philosophie Chimique, professées au Collège de France, par M. Dumas, page 233). But surely such a view is entirely subversive of the atomic theory. It is principally founded on the assumed existence of a similarity between atoms in their capacity for heat, and in their volume while in the gaseous state.

SPECIFIC HEAT OF ATOMS.

The quantity of heat necessary to raise the temperature of equal weights of different bodies a single degree, varies according to their nature, and may be expressed by numbers which are the capacities for heat or specific heats of these bodies (page 49). This difference appears in the numbers for several simple bodies placed together in the first column of the following table, among which no relation can be perceived. But if the comparison is made between the capacity for heat not of *equal* weights, but of *atomic* weights or equivalent quantities of the same bodies, as in the second and third columns of the table, then the numbers for several bodies are found to be nearly the same, and those of others to bear a simple relation to each other.

SPECIFIC HEAT.

	I. Of equal weights. Specific heat of same weight of water being 1.	II. Of atoms. Specific heat of atom of water being 1.	III. Of atoms. Specific heat of atom of lead being 1.	IV. Atomic weights.
Lead	0·0293	0·3372	1·0000	103·56
Tin	0·0514	0·3358	0·9960	58·82
Zinc	0·0927	0·3321	0·9850	32·52
Copper	0·0949	0·3340	0·9908	31·66
Nickel	0·1035	0·3404	1·0095	29·57
Cobalt	0·10696	0·3508	1·040	29·52
Iron	0·1100	0·3315	0·9831	28
Platinum	0·0314	0·3443	1·0211	98·68
Sulphur	0·1880	0·3359	0·9963	16
Mercury	0·0330	0·3714	1·1015	100·07
Tellurium	0·05155	0·3788	1·123	64·14
Gold	0·0298	0·3292	0·9765	98·33
Arsenic	0·081	0·6768	2·0074	75
Silver	0·0557	0·6694	1·9855	108
Phosphorus	0·385	1·3415	3·9789	32
Iodine	0·10824	1·5197	4·506	126·36
Carbon	0·2411	0·1698	0·4766	6
Bismuth	0·03084	0·2190	0·6494	70·95

Of the first twelve substances, which are all metals, with the exception of sulphur, the capacities of the atoms approach so closely, that they may be considered as identical; their capacities appearing to be all nearly one-third of that of the atom of water, in the second column; and nearly coinciding with the capacity of the atom of lead, one of their number in the third column. The weights of the atoms themselves are added in a fourth column, for convenience of reference. The twelve substances in question, taken in the proportions of their atomic weights, will, therefore, undergo an equal change of temperature on assuming an equal quantity of heat. The two metals which follow in the table, namely, arsenic and silver, appear to have an equal capacity for heat, which is double that of lead and the class which coincides with it, while the capacity of phosphorus is four times, and that of iodine four and a half times greater than that of lead and its class. The capacity of the atom of bismuth appears to be two-thirds, and that of carbon to be one-half of the capacity of that of lead. The general results may therefore be stated as follows:—

			Weight of Atom.
Specific heat of atom of	*lead*	1	103·56
“ “	tin	1	58·82
“ “	zinc	1	32·52
“ “	copper	1	31·66
“ “	nickel	1	29·57
“ “	cobalt	1	29·52
“ “	iron	1	28
“ “	platinum	1	98·68
“ “	sulphur	1	16
“ “	mercury	1	100·07
“ “	tellurium	1	64·14
“ “	gold	1	98·33
“ “	arsenic	2	75
“ “	silver	2	108
“ “	phosphorus	4	32
“ “	iodine	4½	126·36
“ “	bismuth	⅔	70·95
“ “	carbon	½	6

Messrs. Dulong and Petit, whose researches supplied the greater portion of these valuable results, drew a more general conclusion from them, namely that all atoms, or at least all simple atoms, have the same capacity for heat, and that those atomic weights which are inconsistent with that supposition, ought to be altered and accommodated to it. The specific heat of a body would thus afford the means of fixing its atomic weight. Some of the alterations in the atomic weights, which would follow the adoption of this law, might be advocated upon other grounds — such as halving the atomic weight of silver, doubling that of carbon, and adding one-half to that of bismuth. But the equivalent of phosphorus would require to be divided by four, while that of arsenic, which it so closely represents in compounds, is divided only by two; changes which are inadmissible.

It must be concluded, then, that elementary atoms have not necessarily the same capacity for heat, although a simple relation appears always to exist between their capacities. The capacities of the three gaseous elements, oxygen, hydrogen, and nitrogen, may likewise be adduced in support of such a relation, provided they are the same for equal volumes of the gases, agreeably to the observations of Dulong. But this relation can only be looked for between bodies while under the same physical condition, and perhaps agreeing in other circumstances also, for the capacity for heat of the same body is known to vary under the different forms of solid, liquid, and gas; and, indeed, while the body is in the same state, its capacity appears not to be absolutely constant, but to increase perceptibly to elevated temperatures (page 49).

The capacities of compound atoms have also been submitted to a sufficiently extensive examination to determine that simple relations subsist among them. In two classes of analogous combinations, the capacities of the atoms for heat were found by M. Neumann, of Königsberg, to approach so closely, that they may be admitted to be the same, the differences being sufficiently accounted for by the errors of observation unavoidable in such delicate researches.

	OF EQUAL WEIGHTS. Specific heat of same weight of water being 1.	OF ATOMIC WEIGHTS. Specific heat of atom of water being 1.
Carbonate of lime	0·2044	0·1148
Carbonate of barytes	0·1080	0·1181
Carbonate of iron	0·1819	0·1156
Carbonate of lead	0·0810	0·1200
Carbonate of zinc	0·1712	0·1187
Carbonate of strontia	0·1445	0.1184
Dolomite (carbonate of lime and magnesia)	0·2111	0·1121
	Mean	0·1162

A small class of sulphates presented a similar result:—

	OF EQUAL WEIGHTS.	OF ATOMIC WEIGHTS.
Sulphate of baryta	0·1068	0·1384
Sulphate of lime	0·1854	0·1412
Sulphate of strontia	0·1300	0·1326
Sulphate of lead	0·0830	0·1398
	Mean	0·1380

The numbers in the second column of both tables deviate very little from their mean, but there is no obvious relation between the two means. Identity in capacity for heat is, therefore, to be looked for in compound atoms of the same nature, and which closely agree in their chemical relations, like the numbers of each group, but not between compound atoms which are differently constituted.

Our information on this subject has been greatly extended of late by the valuable researches of M. Regnault.[1] The *atomic heat* of bodies, as it is named by this chemist, is obtained by multiplying the observed specific heat of each body by its equivalent, the latter being taken upon the oxygen scale. Now this product is found to vary for the metallic elements as the numbers 38 to 42, a greater difference than can result from errors of observation; so that the law of atoms is not verified in an absolute manner. But if it is considered that the atomic weights of the simple substances in question vary at the same time from 200 to 1400, the law must be adopted, as at least closely approximating to the truth. The law would probably represent the results of observation in a perfectly rigorous manner, if the specific heat of each body could be taken at a determinate point of its thermometrical scale, and the specific heat be further disencumbered of all the foreign influences which modify the observation, — such as the state of softness, with the assumption of a certain portion of the latent heat of fusion, which many bodies exhibit before melting entirely, — and the heat absorbed to produce dilatation, which is very great in gases, much more feeble in solid and liquid bodies, but which can in no case be neglected (Regnault). An increase of the density of copper also, produced by hammering it, is found by Regnault to effect a sensible diminution of its specific heat: the latter recovers its original value in the metal after being heated.

The same element, in different conditions as to crystalline form, hardness, and aggregation, may vary greatly in its specific heat, as is observed of carbon both by Regnault, and by Delarive and Marcet. (Annales, &c., t. lxxv. p. 242). The results of the former are as follows:—

SPECIFIC HEAT OF VARIETIES OF CARBON.

Animal charcoal	0·26085
Wood charcoal	0·24150
Coke of coal	0·20307
Charcoal from anthracite	0·20146
Graphite, natural	0·20187
Graphite of iron furnaces	0·19702
Graphite of gas retorts	0·20360
Diamond	0·14687

The calorific capacity of this body is the more feeble in proportion as its state of aggregation is greater: it is an instance of a body which may exist with calorific capacities extending through a very wide range.

The following metallic protoxides of the formula MO,[2] protoxide of lead, red oxide of mercury, protoxide of manganese, oxide of copper, and oxide of nickel, have an atomic heat varying from 70·01 to 76·21, of which the mean is 72.03; these numbers being the observed specific heats of the oxides multiplied by their atomic weights: the same product averages about 40 in the elements. The atomic heat of magnesia is 63·03, and of oxide of zinc, 62·77, expressed in the same manner, which agree very closely together, but differ considerably from the other protoxides.

The protosulphurets, of the formula MS, correspond nearly with the protoxides,— the protosulphurets of iron, nickel, cobalt, zinc, lead, mercury, and tin, varying from 71·34 to 78·34; with a mean of 74·51, while the mean of the protoxides is 72·03.

Sesquioxides, of the formula M_2O_3, give for the product of their specific heats by their atomic weights, numbers between 158·56 and 180·01; with an average of 169·73: they are sesquioxide of iron, sesquioxide of chromium, arsenious acid, oxide

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[1] On the specific heat of simple and compound bodies: Annales de Chimie, &c., t. lxxiii. p. 5, and 3rd sér. t. i. p. 129.

[2] M representing 1 eq. of metal.

of antimony, and oxide of bismuth, represented as Bi_2O_3, with an equivalent of 1003·6. But the number of alumina (Al_2O_3) was different, being in the form of corundum 126·87, and the saphire 139·61. Two corresponding sulphurets gave numbers somewhat higher than the oxides, namely, sulphuret of antimony 186·21, and sulphuret of bismuth 195·90, of which the mean is 191·06.

Two oxides, of the formula MO_2, namely, binoxide of tin, and artificial titanic acid, gave the first 87·23, and the second 86·45. The bisulphuret of iron (pyrites) gave 96·45; the bisulphuret of tin 135·66; the sulphuret of molybdenum 123·46; and bisulphuret of arsenic (AsS_2) 174·51.

Oxides, of the form MO_3, gave the following results: tungstic acid 118·38, molybdic acid 118·96, silicic acid 110·48, boric acid 103·52.

The subsulphuret of copper, Cu_2S, gave 120·21; and the sulphuret of silver, usually represented AgS, gave 115·86.

The following chlorides, to which M. Regnault is disposed to assign the common formula M_2Cl, gave results comprised between 156·83 and 163·42, with a mean of 158·64 — chloride of sodium, chloride of potassium, chloride of silver, subchloride of copper, and subchloride of mercury. The corresponding iodides ranged from 162·30 to 169·38, exclusive of the iodide of silver, which was 180·45. Of corresponding bromides, bromide of potassium was 166·21, bromide of silver 173·31, and bromide of sodium 175·65.

Protochlorides of the formula MCl, namely, chlorides of barium, strontium, calcium, magnesium, lead, mercury, zinc, and tin, were comprised between 114·72 and 119·59; with a mean of 117·03. The protochloride of manganese was somewhat lower, 112·51.

Of volatile bichlorides (MCl_2), bichloride of tin gave 239·18, and chloride of titanium 227·63; of which the mean is 233·40. The two corresponding chlorides of arsenic and phosphorus, MCl_3, gave, the first 399·26, and the second 359·86: mean 379·51.

The numbers for iodide of lead and iodide of mercury (MI) also closely approximate, the first being 122·54, and the second 119·36: mean 120·95. The fluoride of calcium (MF) gave 105·31.

The principal results obtained by M. Regnault for the salts are thrown together in the following table. The equivalents given in the general formula are those of the table at the beginning of this chapter.

Name of the salt.	General formula, (M=1 eq. of metal.)	Product of the specific heats by the atomic weights.	Mean.
Nitrate of potassa	$MO+NO_5$	302·49	301·72
Nitrate of soda	"	297·13	
Nitrate of silver	"	305·55	
Nitrate of barytes	"	248·83	
Metaphosphate of lime	$MO+PO_5$	248·64	
Chlorate of potassa	$MO+ClO_5$	321·04	
Arseniate of potassa	$MO+AsO_5$	317·30	
Pyrophosphate of potassa	$2MO+PO_5$	395·79	389·01
Pyrophosphate of soda	"	382·22	
Phosphate of lead	"	302·14	
Phosphate of lead	$3MO+PO_5$	397·96	
Arseniate of lead	$3MO+AsO_5$	409·37	
Sulphate of potassa	$MO+SO_3$	207·40	206·80
Sulphate of soda	"	206·21	
Sulphate of baryta	"	164·54	166·15
Sulphate of strontia	"	164·01	
Sulphate of lead	"	165·39	
Sulphate of lime	"	168·49	
Sulphate of magnesia	"	168·30	

Name of the salt.	General formula, (M=1 eq. of metal.)	Product of the specific heats by the atomic weights.	Mean.
Chromate of potassa	$MO+CrO_3$	229·83	
Bichromate of potassa	$MO+2CrO_3$	358·67	
Biborate of potassa	$MO+2BO_3$	321·27	311·07
Biborate of soda	“	300·88	
Biborate of lead	“	258·60	
Borate of potassa	$MO+BO_3$	219·52	216·06
Borate of soda	“	212·60	
Borate of lead	“	165·54	
Carbonate of potassa	$MO+CO_2$	187·04	184·35
Carbonate of soda	“	181·65	
Carbonate of lime (Iceland spar)	$MO+CO_2$	131·61	134·40
Carbonate of lime (arragonite)	“	131·56	
Ditto (white saccharoid marble)	“	136·20	
Ditto (grey saccharoid marble)	“	132·45	
Ditto (white chalk)	“	135·57	
Carbonate of baryta	“	135·99	
Carbonate of strontia	“	133·58	
Carbonate of iron	“	138·16	

The results of M. Regnault on the specific heat of compound bodies are of great interest with regard to the question of the division of the atomic weights of certain elements, to which reference has been made. They establish an equally close relation between the specific heat of analogous compounds as exists among elementary bodies. The general law is announced by M. Regnault in the following manner:—"In all compound bodies, of the same atomic composition and similar chemical constitution, the specific heats are in the inverse proportion of the atomic weights." This law comprehends, as a particular case, the law of Dulong and Petit for similar bodies, and appears to be verified by experiment within the same limits as the latter.

RELATION BETWEEN THE ATOMIC WEIGHTS AND VOLUMES OF BODIES IN THE GASEOUS STATE.

Several of the elementary bodies are gases, such as oxygen, hydrogen, nitrogen, and chlorine, and the proportions in which they combine can be determined by *measure*, with equal, if not greater facility than by weight. Now a relation of the simplest nature is always found to subsist between the measures or volumes in which any two of the gaseous elementary bodies unite. This arises from the circumstance that the specific gravities of gases either correspond exactly with their atomic weights, or bear a simple relation to them. The atom of chlorine is 35½ times heavier than that of hydrogen; and chlorine gas is also 35½ times heavier than hydrogen gas, so that the combining measures of these two gases, which correspond with single equivalents, are necessarily equal. The atom of nitrogen, and its weight as a gas, being both 14 times greater than the atom and weight of hydrogen gas, their combining volumes must be the same.. The atom of oxygen is eight times heavier than that of hydrogen, but oxygen gas is 16 times heavier than hydrogen gas, so that taken in equal volumes these two gases are in the proportion by weight of two equivalents of oxygen to one of hydrogen. Hence, in the combination of single equivalents of these elements to form water, half a volume or measure of oxygen gas unites with a whole volume or measure of hydrogen gas. One volume of nitrogen also unites with half a volume of oxygen, and with a whole volume of the same gas, to form respectively the protoxide and deutoxide of nitrogen.

The exact ratio of one to two in which oxygen and hydrogen gases combine by measure, was first observed by Humboldt and Gay-Lussac in 1805. The subject was pursued by the latter chemist, who established the simple ratios in which gases generally combine, and published the laws observed by him, or his Theory of Volumes, shortly after the announcement of the Atomic Theory by Dalton. They afforded new and independent evidence of the combination of bodies in definite and also in multiple proportions, equally convincing as the observed proportions by weight in which bodies unite. Gay-Lussac likewise observed that the product of the union of two gases, if itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from their combination:—thus one volume of nitrogen and one volume of oxygen form two volumes of deutoxide of nitrogen; one volume of chlorine and one volume of hydrogen form two volumes of hydrochloric acid gas; and that when contraction follows combination, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements. Thus two volumes of hydrogen, and one of oxygen, form two volumes of steam; one volume of nitrogen and three of hydrogen gas form two volumes of ammoniacal gas; one volume of hydrogen and one-sixth of a volume of sulphur-vapour form one volume of sulphuretted hydrogen gas. In these and all other statements respecting volumes, the gases compared are supposed to be in the same circumstances as to pressure and temperature.

The uniformity of properties observed among gases in compressibility and dilatability by heat, has appeared to many chemists to indicate a similarity of constitution, and to favour the idea that they all contain the same number of atoms in the same volume. May not equal volumes of oxygen and hydrogen gases, for instance, be represented by an equal number of atoms of oxygen and hydrogen respectively placed at equal distances from each other, and the difference of sixteen to one in the densities of the two gases arise from the atom of oxygen being really sixteen times heavier than that of hydrogen? Equal volumes of gases would then contain an equal number of atoms, and one, two, or three volumes would be an equivalent expression to one, two, or three atomic proportions, the terms *volume* and *atom* becoming of the same import, or expressing equal quantities of bodies. But such a view is obviously inapplicable to compound gases, as their volume has a variable relation to that of their elements; and its adoption would require grave alterations to be made in the atomic weights of several of the elements themselves, to accommodate those weights to the observed densities of the bodies in the gaseous state. This will be seen from the following table, in which the volume or fractional part of a volume placed against each element always contains the same number of its presently received atoms. These volumes are, therefore, the equivalent volumes of the elements, and may be viewed as representing the bulk of their atoms in the gaseous state, *the combining measure of hydrogen being taken as two volumes.*

	ATOMS.	
	Volume.	Weight.
Hydrogen	2	1
Nitrogen	2	14
Chlorine	2	35·5
Bromine	2	98·26
Iodine	2	126·36
Mercury	2	100·07
Oxygen	1	8
Phosphorus	1	32
Arsenic	1	75
Sulphur	$\frac{1}{3}$	16

Of the first six bodies enumerated, equivalent weights occupy each two volumes. It was, indeed, the observation of this equality between the atom and volume in these gases, that led to the supposition of that relation being general. But the atoms of oxygen, phosphorus, and arsenic, occupy only one volume, and would require to be doubled to fill the same volume as the preceding class; or the latter rather preserved fixed, and the former class divided by two. The present atom of sulphur affords only one-third of a volume of vapour, and must, therefore, be multiplied by six to afford two volumes.

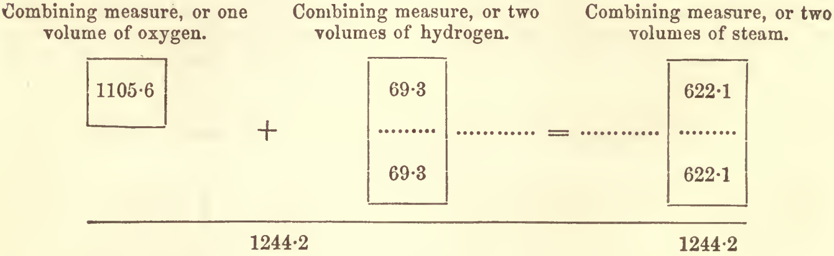
It will be found conducive to perspicuity to apply the expression *combining measure* to the volume or volumes of a gas which enter into combination. The combining measure of oxygen being one volume, the combining measure of hydrogen and its class will be two volumes; or the atom of oxygen gives one, and the atom of hydrogen two volumes of gas. Volumes of the gases may be represented by equal squares with their relative weights inscribed, the numbers having reference to the number assigned to the oxygen volume. If that number be 8, or the atomic weight of oxygen, as in column 1 of the table which follows, then the number to be inscribed in each of the two volumes forming the combining measure of hydrogen will be 0·5, or half its atomic weight, the combining measure itself having the full atomic weight of hydrogen, namely 1. So, of other gases, the combining measure has the whole atomic weight, which is divided among the component volumes. But there is the reason for preferring the number 1105·6 to 8 for the standard oxygen volume, that the weight of a volume of *air* being taken as 1000, that of an equal volume of oxygen is 1105·6; and consequently the corresponding number for the volume of hydrogen, 69·3, expresses the relation in weight of that gas also to air, and so do the corresponding numbers for all the other gases. The numbers on this scale, which express the relative weights of a volume of each gas, and are inscribed in the squares of column 2, are indeed the common *specific gravities of the gases.*

	I.		II.
	Atomic weight.	Combining measure.	Combining measure.
Air			1000
Oxygen	1	8	1105·6
Phosphorus	32	32	4422
Hydrogen	1	0·5 .... 0.5	69·3 .... 69·3
Chlorine	35·5	17·75 .... 17·75	2453 2453

The double squares, which represent the combining measures of hydrogen and chlorine, are divided into volumes by *dotted* lines, to show that the division is imaginary, the partition of a combining measure, like that of an atom which it represents, being impossible. The specific gravities of gases being merely the relative weights of equal volumes, may be expressed by the numbers in the squares of the first column; and the specific gravity of oxygen being accordingly made 8, the specific gravity of any other gas will either be the same number as its atomic weight, or an aliquot part of it. Or if the specific gravity of oxygen be made 1 or 1000, the relation of densities to atomic weights will still be very obvious. (See page 84).

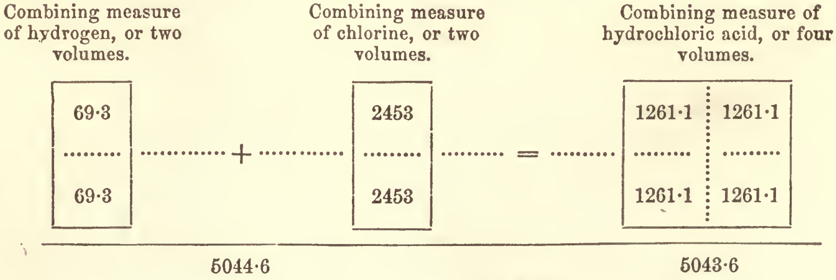
The combining measures of *compound* gases, although variable, have still a constant and simple relation to each other — such as 1 to 1, 1 to 2, or 2 to 3; their elements in combining suffering either no condensation, or a definite and very simple change of volume. Hence the density of a compound gas may often be calculated with more precision from the densities of its constituents, and a knowledge of the change of volume, if any, which occurred in combination, than it can be determined by experiment.

To deduce on this principle the specific gravity of steam. Water consists of single equivalents of oxygen and hydrogen, of which the combining measure of the first is one, and that of the second two volumes. These *three* volumes weigh 1105·6 + 69·3 + 69·3 = 1244·2, and they form *two* volumes of steam; of which one volume must, therefore, weigh 1244·2 divided by two, or 622·1, which is, consequently, the calculated specific gravity of steam, referred to that of air as 1000. The relations in volume of the gases before and after combination may be thus exhibited:—



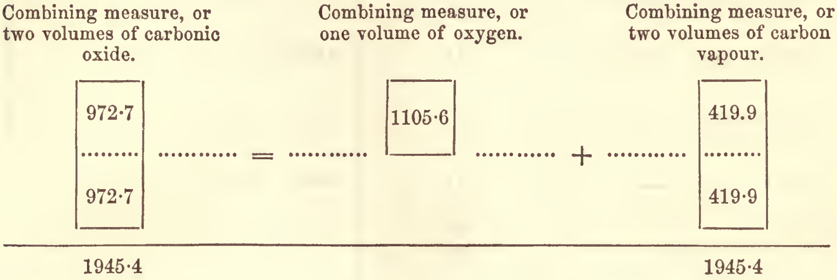
It thus appears necessary to inscribe 622·1 in each volume of steam, to make up 1244·2, the known weight of the two volumes.

In the formation of hydrochloric acid equal measures of chlorine and hydrogen unite without condensation, so that the product possesses the united volumes of its constituent gases.



The specific gravity or weight of a single volume of hydrochloric acid is, therefore, obtained by dividing 5044·6 by 4, and is 1261·1.

The specific gravity of the vapour of an elementary body which there are no means of ascertaining experimentally, may sometimes be calculated from the known density of a gaseous compound containing it. The density of carbon vapour may be thus deduced from the observed density of carbonic oxide gas. Assuming that the combining measure of carbon is double that of oxygen, as is true of hydrogen and several other elementary bodies, then carbonic oxide, which like water consists of single equivalents of its constituents, will resemble steam in its constitution also, and be composed of one volume of oxygen gas, and two volumes of carbon vapour condensed into two volumes. The weight of a single volume of carbonic oxide being 972·7, two volumes (1945·4) may be resolved, as shown in the diagram below, into one volume of oxygen, 1105·6, and two volumes of carbon-vapour, 839·8, (1945·4 — 1105·6 = 839·8) each of which it follows must weigh 419·9, or 420.



But the density 420 thus assigned to carbon vapour will only be true if it corresponds with hydrogen in its combining measure; but the combining measure of carbon vapour may as well be one-half that of hydrogen, like that of phosphorus, or one-sixth, like that of sulphur, and then the density will be double or six times that supposed. The important conclusion, however, that the density of carbon vapour is either 420, or some multiple or sub-multiple of that number, is quite certain.

The following Table comprises nearly all the accurate information which chemists at present possess respecting the specific gravities of gaseous bodies. The bodies placed first in the table are generally considered as belonging to the inorganic, and those in the latter part to the organic department of the science. They are all experimental results, with the exception of two or three cases which are calculated. The specific gravity of carbon-vapour is assumed here as six-sixteenths of that of oxygen (1105·6).

TABLE OF SPECIFIC GRAVITY OF GASES AND VAPOURS.

Names of Substances.	Proportion of an eq. in 1 volume.	Specific Gravity.			Ob-servers.
		Air = 1.	Oxyg. = 1.	H. = 1.	
Sulphur	$3S$	6617	5983·9	96	D.
Oxygen	O	1105·63	1000	16	R.
Phosphorus	P	4355	3938·3	64	D.
Arsenic	As	10600	9586·6	150	M.
Hydrogen	$\frac{H}{2}$	69·26	62·6	1	R.
Carbon (hypothetical)	$\frac{C}{2}$	414·61	375	6	Calcul.
Nitrogen	$\frac{N}{2}$	971·37	878·5	14	R.
Chlorine	$\frac{Cl}{2}$	2421·6	2189·9	35·5	G-L.
Bromine	$\frac{Br}{2}$	5540	5009·7	78	M.
Iodine	$\frac{I}{2}$	8716	7882	126	D.
Mercury	$\frac{Hg}{2}$	6976	6308·5	100·07	D.
Water	$\frac{HO}{2}$	622	562·6	9	R.
Carbonic oxide	$\frac{CO}{2}$	971·2	875	14	Calc.
Protoxide of nitrogen	$\frac{NO}{2}$	1520.4	1375	22	C.
Carbonic acid	$\frac{CO_2}{2}$	1524·5	1378·6	22	B. D.
Chlorocarbonic acid	$\frac{COCl}{2}$	3399	3564.8	49·5	
Sulphide of carbon	$\frac{CS_2}{2}$	2644·7	2391·6	38	G-L.
Hydrosulphuric acid	$\frac{HS}{2}$	1191·2	1077·3	17	G. T.

Names of substances.	Proportion of an eq. in 1 volume.	Specific Gravity.			Ob-servers.
		Air = 1.	Oxyg. = 1.	H. = 1.	
Hypochlorous acid	$\frac{ClO}{2}$	2998·4	2693·4	43·5	
Cyanogen	$\frac{NC_2}{2}$	1806·4	1633·7	26	G-L.
Sulphurous acid	$\frac{SO_2}{2}$	2193	1983·1	32	H-D
Sulphuric acid (anhydrous)..	$\frac{SO_3}{2}$	3000	2713	40	M.
Chlorosulphuric acid	$\frac{SO_2\ Cl}{2}$	4665	4219	67·5	R.
Chloride of sulphur...........	$\frac{SCl_2}{2}$	3685	3332·7	51·5	D.
Arsenious acid	AsO_3	13850	12526	198	M.
Sulphate of water at 848° ...	$\frac{HO,\ SO_3}{2}$	1680	1519	24·5	B.
Chloride of mercury	$\frac{HgCl}{2}$	9800	8862·3	135·5	M.
Bromide of mercury	$\frac{Hg\ Br}{2}$	12160	10996·6	178	M.
Iodide of mercury	$\frac{HgI}{2}$	15630	14134·6	226	M.
Bichloride of tin	$\frac{SnCl_2}{2}$	9199·7	8389·4	...	D.
Bichloride of titanium........	$\frac{TiCl_2}{2}$	6876	6181·9	...	D.
Sulphuret of mercury	$\frac{HgS}{3}$	5510	4982·9	77·3	M.
Penta-chloride of phosphorus	$\frac{PCl_5}{8}$	3680	3329	52·375	C'.
Fluoride of silicium...........	$\frac{SiFl_3}{3}$	3600	3255·5	...	D.
Chloride of silicium...........	$\frac{SiCl_3}{3}$	5939	5370·7	...	D.
Hydrochloric acid	$\frac{HCl}{4}$	1247·4	1128	18·25	B. A.

Names of Substances.	Proportion of an eq. in 1 volume.	Specific Gravity.			Ob-servers.
		Air = 1.	Oxy. = 1.	H. = 1.	
Hydrobomic acid	$\frac{HBr}{4}$	2731	2469·7	39·5	
Hydriodic acid	$\frac{HI}{4}$	4443	4017·8	63·5	G-L.
Hydrocyanic acid	$\frac{HCy}{4}$	947·6	856·9	13·5	G-L.
Chloride of cyanogen	$\frac{Cy\,Cl}{4}$	2111	1908·9	30·75	G-L.
Deutoxide of nitrogen	$\frac{NO_2}{4}$	1038·8	939·3	15	B'.
Peroxide of nitrogen	$\frac{NO_4}{4}$	1720	1555·4	23	C.
Ammonia	$\frac{NH_3}{4}$	596·7	539·6	8·5	B. & A.
Phosphuretted hydrogen	$\frac{PH_3}{4}$	1214	1097·8	17·25	D.
Hydride of arsenic	$\frac{AsH_3}{4}$	2695	2437	39	D.
Terchloride of phosphorus...	$\frac{PCl_3}{4}$	4875	4408·5	69·75	D.
Terchloride of arsenic	$\frac{AsCl_3}{4}$	6300·6	5697·7	91·5	D.
Chloride of bismuth	$\frac{BiCl}{4}$	11160	10092·1	...	J.
Iodide of arsenic	$\frac{AsI_3}{4}$	16100	14560	226·5	M.
Subchloride of mercury	$\frac{Hg_2\,Cl}{4}$	8350	7551	136	M.
Subbromide of mercury	$\frac{Hg_2\,Br}{4}$	10140	9170	180	M.
Fluoride of boron	$\frac{BF_3}{4}$	2312·4	2091·2	...	J-D.
Chloride of boron	$\frac{BCl_3}{4}$	3942	3564·8	...	D.
Carburetted hydrogen	$\frac{C_2\,H_4}{4}$	559·6	506·1	8	

Names of substances.	Proportion of an eq. in 1 volume.	Specific Gravity.			Observers.
		Air = 1.	Oxyg. = 1.	H. = 1.	
Methylene (?)	$\frac{C_2H_2}{4}$	490	443	7	
Olefiant gas	$\frac{C_4H_4}{4}$	985·2	891	14	T. S.
Oil gas	$\frac{C_8H_8}{4}$	1892	1711	28	F.
Cetene	$\frac{C_{32}H_{32}}{4}$	8007	7240·8	112	D. P.
Oléene	$\frac{C_{12}H_{12}}{4}$	2875	2600·8	42	F".
Elœene	$\frac{C_{18}H_{18}}{4}$	4071	3681·5	63	F'.
Amilene	$\frac{C_{20}H_{20}}{4}$	5061	4576·6	70	C".
Naphthaline	$\frac{C_{20}H_8}{4}$	4528	4072	64	D.
Paranaphthaline	$\frac{C_{30}H_{12}}{4}$	6741	6096	96	D.
Benzene (benzole)	$\frac{C_{12}H_6}{4}$	2770	2505	39	M.
Terebene	$\frac{C_{20}H_{16}}{4}$	4765	4309	68	D.
Citrene	$\frac{C_{20}H_{18}}{4}$	4891	4422·8	68	C".
Retinaphtha	$\frac{C_{14}H_8}{4}$	3230	2921	46	P. W.
Retinile	$\frac{C_{18}H_{12}}{4}$	4242	3836	60	P. W.
Retinole	$\frac{C_{32}H_{16}}{4}$	7110	6429·7	104	P. W.
Sweet oil of wine	$C_{10}H_8$	9476	8569·3	136	R.
Volatile sweet oil of ether	$\frac{C_8\ H_9}{2}$	3965	3582	57	M.
Mesitylene	$\frac{C_{12}H_8}{4}$	2805	2836·5	40	C".

Names of Substances.	Proportion of an eq. in 1 volume.	Specific Gravity.			Observers.
		Air = 1.	Oxy. = 1.	H. = 1.	
Wood-spirit	$\frac{C_2H_4O_2}{4}$	1120	1012·8	16	D. P.
Methylic ether	$\frac{C_2H_3O}{2}$	1617	1462·3	23	*Id.*
Methylic ether (monochlorinated)	$\frac{C_2H_2ClO}{2}$	3903	3529·5	57·5	R.
Methylic ether (bichlorinated)	$\frac{C_2HCl_2O}{6}$	2115	1912·6	30·66	R.
Methylic ether (perchlorinated)	$\frac{C_2Cl_3O}{3}$	4670	4223·2	62·75	*Id.*
Formic acid at 321°·8 F.	$\frac{C_2H_2O_4}{4}$	1610	1456	23	B.
Sulphide of methyl	C_2H_3S	6367	5557·8	94	*Id.*
Chloride of carbon	$\frac{C_2Cl_4}{4}$	5330	4820	77	R.
Chloride of carbon (another)	$\frac{C_4Cl_4}{4}$	5820	5263·1	83	*Id.*
Chloride of carbon (another)	$\frac{C_4Cl_6}{4}$	8157	7376·5	118·5	*Id.*
Chloride of methyl	$\frac{C_2H_3Cl}{4}$	1731	1565·4	25·25	D. P.
Chloride of methyl (monochlorinated)	$\frac{C_2H_2Cl_2}{4}$	3012	2724	42·5	R.
Fluoride of methyl	$\frac{C_2H_3F}{4}$	1186	1072·5	16·5	D. P.
Iodide of methyl	$\frac{C_2H_3I}{4}$	4883	4415·8	70·5	*Id.*
Sulphate of methyl	$\frac{C_2H_3O, SO_3}{2}$	4565	4128·1	63	*Id.*
Nitrate of methyl	$\frac{C_2H_3O, NO_5}{2}$	2653	2399·6	38·5	*Id.*
Formiate of methyl	$\frac{C_2H_3O, C_2HO_3}{4}$	2084	1884·5	30	*Id.*
Acetate of methyl	$\frac{C_2H_3O, C_4H_3O_3}{4}$	5563	2317·7	37	*Id.*

Names of substances.	Proportion of an eq. in 1 volume.	SPECIFIC GRAVITY.			Observers.
		Air = 1.	Oxyg. = 1.	H. = 1.	
Methylal	$\frac{C_6H_8O_4}{4}$	2625	2374	38	M'.
Alcohol	$\frac{C_4H_6O_2}{4}$	1613	1458·7	23	G-L.
Mercaptan	$\frac{C_4H_6S_2}{4}$	2326	2103·4	31	B.
Ether	$\frac{C_4H_5O}{2}$	2586	2338·5	37	G-L.
Sulphuret of ethyl	$\frac{C_4H_5S}{2}$	3100	2803·4	45	R.
Chloride of ethyl	$\frac{C_4H_5Cl}{4}$	2299	2006·6	42·25	T.
Chloride of ethyl (monochlorinated)	$\frac{C_4H_4Cl_2}{4}$	3478	3145·2	49·5	R.
Chloride of ethyl (bichlorinated)	$\frac{C_4H_3Cl_3}{4}$	4530	4096·5	66·75	R.
Chloride of ethyl (trichlorinated)	$\frac{C_4H_2Cl_4}{4}$	5799	5244·1	84	*Id.*
Chloride of ethyl (quadrichlorinated)	$\frac{C_4HCl_5}{4}$	6975	6307·6	101·25	*Id.*
Iodide of ethyl	$\frac{C_4H_5I}{4}$	5475	4951·2	77·5	G-L.
Nitrous ether	$\frac{C_4H_5O,\ NO_3}{4}$	2626	2374·7	37·5	D. B'.
Chlorocarbonic ether	$\frac{C_4H_5O,\ C_2O_3Cl}{4}$	3829	3462·6	54·25	D.
Sulphurous ether	$\frac{C_4H_5O,\ SO_2}{2}$	4780	4323	69	E. & B.
Oxalic ether	$\frac{C_4H_5O,\ C_2O_3}{2}$	5087	4600·3	73	D. B'.
Silicic ether (tribasic)	$\frac{3C_4H_5O,\ SiO_3}{3}$	7210	6521	104	E.
Boric ether (tribasic)	$\frac{3C_4H_5O,\ BO_3}{4}$	5140	4649	72	E. & B.
Acetic ether	$\frac{C_4H_5O,\ C_4H_3O_3}{4}$	3067	2773·5	44	*Id.*

Names of Substances.	Proportion of an eq. in 1 volume.	Specific Gravity.			Observers.
		Air = 1.	Oxy. = 1.	H. = 1.	
Benzoic ether	$\frac{C_4H_5O,\ C_{14}H_5O_2}{4}$	5409	4899	71	*Id.*
Succinic ether	$\frac{C_4H_5O,\ C_4H_3O_3}{2}$	6220	5624·8	87	A.
Pyromucic ether	$\frac{C_4H_5O,\ C_{10}H_3O_5}{4}$	4859	4394·1	70	M.
Œnanthic ether	$\frac{C_4H_5O,\ C_{14}H_{13}O_2}{2}$	10508	9502·5	150	L. & P.
Dutch liquid	$\frac{C_4H_3Cl,\ HCl}{4}$	3443	3113·5	49·5	G-L. D.
Bromide of olefiant gas	$\frac{C_4H_3Br,\ HBr}{4}$	6485	5864·5	94	R.
Chloral	$\frac{C_4HCl_3O_2}{4}$	5130	4639·1	73·75	D.
Chloroform	$\frac{C_4HCl_3}{4}$	4199	3797·2	65·78	D.
Aldehyde	$\frac{C_4H_4O_2}{4}$	1532	1385·4	22	L.
Alcarsin	$\frac{C_4H_6As}{2}$	7184	6496·6	105	B.
Acetic acid at 482° F.	$\frac{C_4H_4O_4}{4}$	2080	1879·8	30	C”.
Chloracetic acid	$\frac{C_4HCl_3O_4}{4}$	5300	4792·9	81·75	D.
Acetone	$\frac{C_6H_6O_2}{4}$	2019	1825·8	29	*Id.*
Benzoic acid	$\frac{C_{14}H_6O_4}{4}$	4270	3861·4	61	D. M.
Hydride of salicyl	$\frac{C_{14}H_6O_4}{4}$	4276	3867·1	61	P.
Eugenic acid	$\frac{C_{20}H_{12}O_5}{4}$	6400	5787·6	86	D.
Camphor	$\frac{C_{20}H_{16}O_2}{4}$	5468	4945·7	76	*Id.*
Urethane	$\frac{C_6NH_7O_4}{4}$	3096	2800	44·5	*Id.*

After the name of each substance in the preceding table is given the formula of its equivalent, which is divided by the number of volumes of vapour which the equivalent gives and the combining measure contains. The equivalent thus divided therefore expresses the composition of a single volume of the vapour. The first column of numbers contains the specific gravities referred to air as 1000; the second, in which the specific gravities are expressed with reference to that of oxygen as 1000, is obtained by dividing the former specific gravities by 1105·6, the specific gravity of oxygen gas. In the third column, the specific gravities are referred to hydrogen as 1; and consequently the number for any vapour expresses how many times that vapour is heavier than hydrogen. The numbers of this column only are obtained by calculation from the equivalents, and are therefore the theoretical densities: if divided by 16 they give corresponding theoretical densities on the scale of oxygen equal to 1; or if divided by 14·416 (the number of times which air is heavier than hydrogen) they give the theoretical densities on the scale of air equal to 1. The letter or letters in the last column refer to the name of the observer on whose authority the experimental specific gravities of the first and second columns of numbers are given.[1]

An extraordinary variation in the specific gravity of acetic acid at different temperatures was observed by M. Dumas, which is confirmed by M. Cahours and M. Bineau, (Annales de Chimie, &c. 3^{e} sér. t. xviii. p. 226), and the anomaly found to extend to certain acids allied to the acetic; namely formic, butyric, and valerianic acids. Thus the vapour of acetic acid ($H\,O, C_4\,H_3\,O_3$), has a specific gravity of 3200 at 125° Centig., 2480 at 160° C., 2220 at 200°, 2090 at 230°, 2080 at 250°, and retains the last specific gravity, which corresponds with the theoretical density of four volumes from one equivalent, at higher temperatures; the observation being made up to 338° C. This vapour has, indeed, been observed with a density so great as 3950, under reduced pressure, and at a low temperature, namely 69° Fahr. The variation is probably accounted for by considering the acid to be bibasic at low temperatures, with a double equivalent and double density, and to assume progressively the molecular form and single density of the monobasic acid, as the temperature rises. The acid undergoes no permanent or constitutional alteration at the highest of the temperatures specified, but condenses again in possession of all its usual properties.

Butyric acid has a density of 3680 at 177° C., which falls to 3070 at 261° C., and remains the same at 330° C. Valerianic acid gave similar results, but the variation was less excessive (Cahours).

Formic acid vapour was observed by M. Bineau with a specific gravity as high as 3230, under a pressure of about one-fiftieth of an atmosphere, and at the temperature of 51° F., while it rarefied to 1610 at 416° Fahr., under the usual atmospheric pressure. The two sorts of molecular groups of this acid correspond respectively with the specific gravities, 1590 and 3180; in the first case the ordinary equivalent ($C_2\,H\,O_3 + H\,O$) gives four, and in the second two equivalents of vapour.

The acetic and other acids of this class were formerly supposed to give three volumes of vapour, but it is doubted whether the proportions of three and six volumes exist at all, or that the vaporous molecule of compound bodies is ever divisible except by 2, 4, or 8. Three compounds of silicium form exceptions to this rule—the chloride $Si\,Cl_3$, and the corresponding fluoride and ether, which give three volumes. From this circumstance, and the analogy which subsists between silicic acid, and the titanic acid and binoxide of tin, it has been proposed to diminish the

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[1] A signifies Felix d'Arcet; B, Bunsen; B', Berard; BA, Biot and Arago; BD, Berzelius and Dulong; C, Colin; C', Cruikshanks; C'', Cahours; D, Dumas; DB, Dumas and Boussingault; DB', Dumas and P. Boullay; DP, Dumas and Peligot; E, Ebelmen; E and B, Ebelmen and Bouquet; F', Fremy; G-L, Gay-Lussac; GT, Gay-Lussac and Thenard; L, Liebig; LP, Liebig and Pelouze; M, Mitscherlich; M', Malaguti; P, Piria; PW, Peletier and Walter; R, Regnault; TS, Theodore de Saussure. The table itself is that given by M Baudrimont in his excellent Traité de Chimie, somewhat modified and extended.

equivalent of silicium one-third, representing silicic acid by Si O_2; and, in consequence, the chloride and fluoride of silicium and silicic ether would possess, in the state of vapour, a molecule divisible by 2. Two chlorinated compounds of methyl and the sulphuret of mercury are the only other substances of which the equivalents are divided in the table by 6 or 3.

The specific gravity of the vapour of oil of vitriol H O, S O_3, was found to vary from 2500 at 630° Fahr., to 1680 at 928° Fahr. This substance should have a density of 1640 on the hypothesis of the union of the anhydrous acid and water without condensation; a number which corresponds sufficiently well with observations of the density made at temperatures above 750° Fahr. But the vapours of the acids are not the only bodies which present such anomalies; the oils of aniseed and fennel, which are perfectly neutral, offer similar results. Thus the vapour of the oil of aniseed varies in specific gravity from 5980 at 473° Fahr. to 5190 at 640° Fahr.; its theoretical density being 5180. The greater part, however, of the compound ethers, and a large number of the volatile oils, particularly the pure hydrocarbon oils, furnish, at from 60 to 80 degrees above the boiling point, numbers which accord closely with theory.

The specific gravity of the pentachloride of phosphorus, taken by M. Mitscherlich at 335° Fahr., is represented by 4850, which led to the conclusion that the molecule of this compound gives six volumes of vapour. But M. Cahours finds that the density of this vapour varies with the temperature, from 4990 at 374° to 3656 at 621°: about 554° the density is 3680, which corresponds with eight volumes of vapour.

From these tables, it appears that a simple relation always subsists between the combining measures of different bodies in the gaseous state:

That the combining measure of a few bodies is the same as that of oxygen, or *one volume;* of a large number, double that of oxygen, or *two volumes;* and of a still larger number, four times that of oxygen, or *four volumes;* while combining measures of other numbers of volumes, such as *three* and *six*, or of fractional portions of one volume, such as *one-third,* are comparatively rare:

That the specific gravity of a gas may be calculated from its atomic weight, or the atomic weight from the specific gravity, as they are necessarily related to each other. Thus, to find the specific gravity of a vapour like that of phosphorus, of which the combining measure is one volume, or the same as that of oxygen. The specific gravities of two bodies, of which the *volumes* of the atoms are the same, must obviously be as the *weights* of these atoms. Hence, 8 and 32 being the atomic weights of oxygen and phosphorus, and 1105·6, the known specific gravity of oxygen, the specific gravity of phosphorus vapour is obtained by the following proportion—

$$8 : 32 :: 1105{\cdot}6 : 4422$$

= sp. gr. of phosphorus vapour.

Secondly, to find the specific gravity of a vapour like that of fluorine, of which the combining measure is assumed to be two volumes, or double that of oxygen. The atomic weight of fluorine 18·70,

$$8 : 18{\cdot}70 :: 1105{\cdot}6 : 2584{\cdot}34 =$$

twice the specific gravity of fluorine, being the weight of two volumes, and the specific gravity required is 1292·17.

These cases are examples of a general rule, that the specific gravity of a body in the state of vapour is obtained by multiplying the atomic weight of the body by 1105·6, the specific gravity of oxygen, and dividing by 8. The number thus found must then be divided by the number of volumes which are known to compose the combining measure of vapour.

The specific gravities thus calculated are generally more accurate than those obtained by direct experiment, from the circumstance that the operation of taking the specific gravity of a gas is generally less susceptible of precision, than the chemical analyses on which the atomic weights are founded. The densities of vapours, taken only a few degrees above their condensing points, are generally a little greater than the truth, owing to a peculiarity in their physical constitution which was formerly explained (page 81). Of such bodies, therefore, the theoretical is a necessary check upon the experimental density.

SECTION IV.—RELATION BETWEEN THE CRYSTALLINE FORM AND ATOMIC CONSTITUTION OF BODIES—ISOMORPHISM.

Bodies on passing from the gaseous or liquid to the solid state generally present themselves in crystals, or regular geometrical figures, which are the larger and more distinct the more slowly and gradually they are produced. Their formation is readily observed in the spontaneous evaporation of a solution of sea-salt, or in the slow cooling of a hot and saturated solution of alum, which salts assume the forms of the cube and regular octohedron. The crystalline form of a body is constant, or subject only to certain geometrical modifications which can be calculated, and is most serviceable as a physical character for distinguishing salts and minerals. Between bodies of similar atomic constitution, a relation in form has been observed of great interest and beauty, which now forms a fundamental doctrine of physical science, like the subjects of atomic weights and volumes just considered.

Gay-Lussac first made the remark that a crystal of potash-alum transferred to a solution of ammonia-alum continued to increase without its form being modified, and might thus be covered with alternate layers of the two alums, preserving its regularity and proper crystalline figure. M. Beudant afterwards observed that other bodies, such as the sulphates of iron and copper, might present themselves in crystals of the same form and angles, although the form was not a simple one like that of alum. But M. Mitscherlich first recognised this correspondence in a sufficient number of cases to prove that it was a general consequence of similarity of composition in different bodies. To the relation in form he applied the term *isomorphism*, (from ἴσος, equal, and μορφή, shape), and distinguished bodies which assume the same figure as *isomorphous*, or (in the same sense) as *similiform* bodies. The law at which he arrived is as follows:—"The same number of atoms combined in the same way produce the same crystalline form; and crystalline form is independent of the chemical nature of the atoms, and determined only by their number and relative position."

This law has not been established in all its generality, but perhaps no fact is certainly known which is inconsistent with it, while an indisposition which certain classes of elements have to form compounds at all similar in composition to those formed by other classes, limits the cases for comparison, and makes it impossible to trace the law, throughout the whole range of the elements, in the present state of our knowledge respecting them.

The relation of isomorphism is most frequently observed between salts, from their superior aptitude to form good crystals. Thus the arseniate and phosphate of soda are obtained in the same form, and are exactly alike in composition, each salt containing one proportion of acid, two of soda, and one of water as bases, together with twenty-four atoms of water of crystallization. With a different proportion of water of crystallization, namely, with fourteen atoms, and the other constituents unchanged, the crystalline form is totally different, but is again the same in both salts. For every arseniate, there is a phosphate corresponding in composition, and identical in form; the isomorphism of these two classes of salts is indeed perfect. The arsenic and phosphoric acids contain each five proportions of oxygen to one of arsenic and phosphorus respectively, and are supposed to be themselves isomorphous, although the fact cannot be demonstrated, as the acids do not crystallize. The elements, phosphorus and arsenic, are also known to be isomorphous: and the isomorphism of their acids and salts is referred to the isomorphism of the elements themselves; isomorphous compounds in general appearing to arise from isomorphous elements uniting in the same manner with the same substance.

The isomorphism of the sulphate, seleniate, chromate, and manganate of the same base is likewise clear and easily observed; each of the acids in these cases containing three proportions of oxygen to one of selenium, sulphur, chromium, and manganese, themselves presumed to be isomorphous.

Of bases, the isomorphism of the class consisting of magnesia, oxide of zinc, oxide of cadmium, and the protoxides of nickel, iron and cobalt, is well marked in the salts which they form with a common acid, and is particularly observable in the double salts of these oxides, such as the sulphate of magnesia and potassa, sulphate of zinc and potassa, sulphate of copper and potassa, which have all six atoms of water and a common form. The sulphates themselves of these bases differ, most of them affecting seven atoms of water of crystallization, while the sulphate of copper affects five; but those with the seven may likewise be crystallized in favourable circumstances with five atoms of water, and then assume the form of the copper salt, thus exhibiting a second isomorphism like the arseniate and phosphate of soda.

The sesquioxides of the same class of metals with alumina and the sesquioxide of chromium, which consist of two atoms of metal and three of oxygen, also afford an instructive example of isomorphism, particularly in their double salts. The sulphate of the sesquioxide of iron with sulphate of potassa and twenty-four atoms of water, forms a double salt having the octohedral form of sulphate of alumina and potassa, or common alum, the same astringent taste, with other physical and chemical properties so similar, that the two salts can with difficulty be distinguished from each other. The salt is called iron alum, and there are corresponding manganese and chrome alums, neither of which contains alumina, but the sesquioxide of manganese and sesquioxide of chromium in its place, with the proportions of acid and water which exist in common alum. In all these salts another substitution may occur without change of form; namely, that of soda or oxide of ammonium for the potassa in the sulphate of potassa, giving rise to the formation of what are called soda and ammonia alums.

Certain facts have been supposed to militate against the principles of isomorphism, which require consideration.

1. It appears that the corresponding angles of crystals reputed isomorphous are not always exactly equal, but are sometimes found to differ two or three degrees, although the errors of observation in good crystals rarely exceed 10′ or 20′ of a degree. But it has been shown by Mitscherlich that a difference may exist between the inclinations of two series of similar faces in different specimens of the same salt, of 59′; while it is also known that the angles of a crystal alter sensibly in their relative dimensions with a change of temperature (page 34). The angles of crystals are, therefore, affected in their values within small limits by causes of an accidental character, and absolute identity in crystalline form may require the concurrence of circumstances which are not found together in the ordinary modes of producing many crystals, which are still truly isomorphous.

The following table exhibits the inequalities which have been observed between the angles of certain isomorphous crystals:—

Rhomboidal form.

Carbonate of	manganese (diallogite)	103°
“	lime (calc-spar)	105° 5′
“	lime and magnesia (dolomite)	106° 15′
“	magnesia (giobertite)	107° 25′
“	iron (spathic iron)	107°
“	zinc (smithsonite)	107° 40′

Square prismatic with rhomboidal base.

Carbonate of	lime (arragonite)	116° 5′
“	lead (ceruse)	117°
“	strontia (strontianite)	117° 32′
“	baryta (witherite)	118° 57′

Sulphate of	baryta	101° 42′
"	lead (anglesite)	103° 42′
"	strontia (celestine)	104° 30′

2. It appears that the same body may assume in different circumstances two forms which are totally dissimilar, and have no relation to each other. Thus sulphur on crystallizing from solution in the bisulphide of carbon or in oil of turpentine, at a temperature under 100°, forms octohedrons with rhombic bases, but when melted by itself and allowed to cool slowly, it assumes the form of an oblique rhombic prism on solidifying at 232°. These are incompatible crystalline forms, as they cannot be derived from one common form. Carbon occurs in the diamond in regular octohedrons, and in graphite or plumbago in six-sided plates, forms which are likewise incompatible. Sulphur and charcoal have each, therefore, two crystalline forms, and are said to be *dimorphous*, (from δις, twice, and μορφὴ, shape). Carbonate of lime is another familiar instance of dimorphism, forming two mineral species, calc-spar and arragonite, which are identical in composition, but differ entirely in crystalline form. G. Rose has shown that the first or second of these forms may be given to the granular carbonate of lime formed artificially, according as it is precipitated at the temperature of the air, or near the boiling point of water. Of its two forms, carbonate of lime most frequently affects that of calc-spar: but carbonate of lead, which assumes the same two forms, and is therefore isodimorphous with carbonate of lime, chiefly affects that of arragonite, and is very rarely found in the other form. Had these carbonates, therefore, been each known only in its common form, their isomorphism would not have been suspected,—an important observation, as the want of isomorphism between certain other bodies may be caused by their being really dimorphous, although the two forms have not yet been perceived. Crystallization in three forms is not unknown: thus titanic acid is found in three distinct forms, as the minerals rutile, brookite, and anatase.

3. The observation of the isomorphism of bodies is of the greatest value as an indication that they possess a similar constitution, and contain a like number of atoms of their constituents. But it must be admitted that the most perfect coincidence in form is likewise observed between certain bodies which are quite different in composition. Thus bisulphate of potassa is dimorphous, and crystallizes in one of the two forms of sulphur (Mitscherlich). Nitrate of potassa in common nitre has the form of arragonite, and occurs also, there is reason to believe, in microscopic crystals in the form of calc-spar. Nitrate of soda, again, has the form of calc-spar. Permanganate of baryta and the anhydrous sulphate of soda likewise crystallize in one form. Between the first pair, sulphur and bisulphate of potassa, the absence of all analogy in composition is sufficiently obvious, notwithstanding their isomorphism. Between nitrate of potassa and carbonate of lime, and between permanganate of baryta and sulphate of soda, there is no similarity of composition, on the ordinary view which is taken of the constitution of these salts, but both of these pairs have been assimilated, in speculative views of their constitution proposed by Mr. Johnston (Philos. Mag. third series, vol. xii. page 480) in regard to the first pair, and by Dr. Clark (Records of General Science, vol. iv. page 45) in regard to the second, which merit consideration, although the hypotheses cannot be both correct, as they are based upon incompatible data. To these may be added, the sulphate of baryta with perchlorate and permanganate of potassa: BaO, SO_3 with KO, ClO_7 and $KO, Mn_2 O_7$. The sulphide of antimony with sulphate of magnesia: $Sb S_3$ with $MgO, SO_3 + 7HO$. Borax with augite, labradorite and anorthite, quartz and chabasite, mohsite and eudialite, anatase and apophyllite, zircon and wernerite, manganite and prehnite. Copper pyrites, $Cu Fe S_2$, has also the same form as braunite or sesquioxide of manganese, $Mn_2 O_3$. Leucite and analcime both belong to the regular system, and are aluminous silicates of similar composition; but, while the first contains one equivalent of potassa, the other contains one equivalent of soda $+ 2HO$.

The nitrite of lead has the same octohedral figure as the nitrate of lead, with two atoms of oxygen less in its acid.

Of examples of identity of crystalline form without any well-established relation in composition, many others might be quoted, if occurrence in the simple forms of the cube and regular octohedron should be allowed to constitute isomorphism. For example: carbon, sea-salt, arsenious acid, galena, the magnetic oxide of iron, and alum, all occur in octohedrons, although they are no way related in composition. But these simple forms are so common, that they can be held as affording no proof of isomorphism, unless in cases where it is to be expected from admitted similarity of composition, as between the different alums, or between chrome iron and the magnetic oxide of iron, $Cr_2 O_3$, FeO and $Fe_2 O_3$, FeO.

But notwithstanding the occurrence of such apparently fortuitous coincidences in form, isomorphism must still be considered as the surest criterion of similarity of composition which we possess. Truly isomorphous bodies generally correspond in a variety of other properties besides external form. Arsenic and phosphorus resemble each other remarkably in odour, although the one is a metal and the other a non-metallic body, while the corresponding arseniates and phosphates agree in taste, in solubility, in the degree of force with which they retain water of crystallization, and in various other properties. The seleniate and sulphate of soda, with ten atoms of water, which are isomorphous, are both efflorescent salts, and correspond in solubility, even so far as to agree in an unwonted deviation from the usually observed increasing rate of solubility at high temperatures, both salts being more soluble in water at 100° than at 212°. In fact, isomorphism appears to be always accompanied by many common properties, and to be the feature which indicates the closest relationship between bodies.

It will afterwards appear that the more nearly bodies agree in composition, they are the more likely to act as solvents of each other, or to be miscible in the liquid form. An attraction for each other of the same character is probably the cause of the easy blending together of the particles of isomorphous bodies, and of the difficulty of separating them after they are once dissolved in a common menstruum; such isomorphous salts as the permanganate and perchlorate of potassa may, indeed, crystallize apart from the same solution, owing to a considerable difference of solubility; and potassa-alum may be purified, in a great measure, by crystallization, from iron-alum, which is more soluble, and remains in the mother-liquor; but most isomorphous salts, such as the sulphates of iron and copper, or the iodide and chloride of potassium, when once dissolved together, do not crystallize apart, but compose homogeneous crystals, which are mixtures of the two salts in indefinite proportions. This intermixture of isomorphous compounds is of frequent occurrence in minerals, and was quite inexplicable, and appeared to militate against the doctrine of combination in definite proportions, till the power of isomorphous bodies to replace each other in compounds was recognized as a law of nature. Thus, in garnet, which is a silicate of alumina and lime, Al_2O_3, $SiO_3+3CaO\ SiO_3$, the alumina is found often wholly or in part replaced by an equivalent quantity of peroxide of iron; while the lime, at the same time, may be exchanged wholly or in part for protoxide of iron, or for magnesia, without the proper crystalline character of the mineral being destroyed. Hence the composition of mineral species is most properly expressed by general formulæ, where a letter, such as R, expresses an equivalent of metal which may be calcium, magnesium, manganese, iron, &c. :—

The Pyroxenes by $3RO, 2SiO_3$.
The Epidotes by $3RO, 2Al_2O_3, 3SiO_3$.

⁂ The various forms of crystals were first happily described by Professor Weiss, of Berlin, by reference to "crystalline axes," which are three straight lines passing through the same point, and terminating in the surfaces or angles of the crystal. The simplest case is that in which the three axes cross each other at right angles, and are equal in length, as represented (fig. 53); *c* being the vertical, and *a* and *b* the two horizontal axes. A crystal is formed by applying planes in three principal ways to these axes.

1. By applying six planes so that each shall be perpendicular to one axis and parallel to the other two, the hexahedron, or, as it is more commonly termed, the cube (fig. 54), is formed. Here the axes terminate in the centre of each of the six faces of the crystal.

FIG. 53.

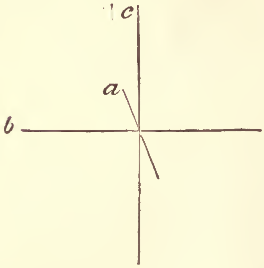
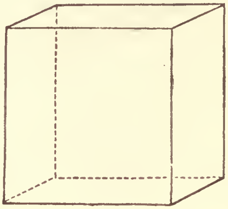


FIG. 54.



2. By applying one plane to an extremity of each of the three axes, as to the points *a*, *b*, and *c* (fig. 63), and seven planes in the same manner to other extremities, the regular octohedron is produced, of which the eight faces or planes are all equilateral triangles (fig. 55). The axes here terminate in the angles of the crystal.

3. The plane may be applied to the extremities of two axes, and be parallel to the third, which will require twelve planes to close the figure, and give rise to the rhombic dodecahedron (fig. 56).

FIG. 55.

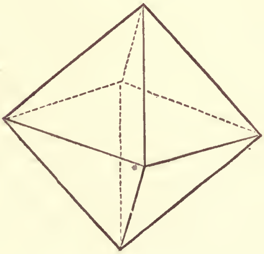
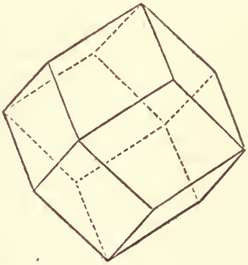


FIG. 56.



In these three principal forms, the planes are applied to the axes at equal distances from the centre. They may also cut the axes at unequal distances from the centre, giving rise to four other less usual forms.

A body in crystallizing may assume any of these forms, the only thing constant being the crystalline axes. Hence common salt crystallizes both in the cube and octohedron, although most usually in the former figure; and the magnetic oxide of iron both in the octohedron and rhombic dodecahedron. A body may even assume several of these forms at the same time; that is, may present at once faces of the cube, octohedron, and dodecahedron. Of the octohedral crystals of alum, for instance, the solid angles are always found to be cut or truncated by planes which belong to the cube of the same axes (fig. 57); and the edges of the octohedron in the same salt are sometimes removed or bevelled by the faces of the dodecahedron (fig. 58). Fig. 59 represents a combination of all these three forms; and similar or even more complicated combinations are often found in nature.

Fig. 57.

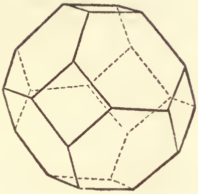


Fig. 58.

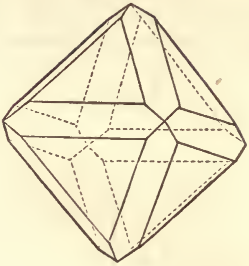
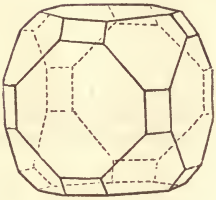


Fig. 59.



The groups of forms thus associated, by being deducible from the same axes, constitute what is called a "system of crystallization." Six such systems are enumerated by Weiss, to some one of which every crystalline body belongs.

1. The octohedral or regular system of crystallization, with the three principal axes at right angles to each other, and equal in length. It is that already described.

2. The square prismatic, with the axes at right angles, but two only of them equal in length.

3. The right prismatic, with the axes at right angles, but unequal in length.

4. The rhombohedral, with the axes equal, and crossing at equal but not right angles.

5. The oblique prismatic, with two of the axes intersecting each other obliquely, while the third is perpendicular to both, and unequal in length.

6. The doubly-oblique prismatic, with all three axes intersecting each other obliquely, and unequal.

By the apposition of planes to these different sets of crystalline axes, in the same modes as to the axes of the regular system, series of forms are produced, having a general analogy in all the systems, but specifically different.

For additional information on the subject of crystallography, which, although highly important to the chemical inquirer, is not exactly a department of chemistry, reference may be made to the Essay of Dr. Whewell, in the Phil. Trans. for 1825; to an Essay by Dr. Leeson, in the Memoirs of the Chemical Society, vol. iii.; the German Elements of Crystallography of G. Rose; the Systems of Crystallography of Professor Miller and Mr. J. J. Griffin; and to a short work lately published, entitled "Elements de Crystallographie, par M. J. Müller, traduits de l'Allemand par Jerome Nickles," which appears to be well adapted to the wants of the chemist. A full list of isomorphous substances is given by M. Gmelin in his invaluable *Handbuch der Chemie*, vol. i. p. 83.

CLASSIFICATION OF ELEMENTS.

The extent to which the isomorphous relations of bodies have been traced, will appear on reviewing the groups or natural families in which the elements may be arranged, and observing the links by which the different groups themselves are connected; these classes not being abruptly separated, but shading into each other in their characters, like the classes created by the naturalist for the objects of the organic world.

I. *Sulphur Class.*—This class comprises four elementary bodies: oxygen, sulphur, selenium, tellurium. The three last of these elements exhibit the closest parallelism in their own properties, in the range of their affinities for other bodies, and in the properties of their analogous compounds. They all form gases with one atom of hydrogen, and powerful acids with three atoms of oxygen, of which the salts, the sulphates, seleniates, and tellurates are isomorphous; and the same relation undoubtedly holds in all the corresponding compounds of these elements.

Oxygen has not yet been connected with this group by a certain isomorphism of any of its compounds; but a close correspondence between it and sulphur appears, in their compounds with one class of metals being alkaline bases of similar properties, forming the two great classes of oxygen and sulphur bases, such as oxide of potassium and sulphide of potassium; and in their compounds with another class of elements being similar acids, giving rise to the great classes of oxygen and sulphur acids, such as arsenious and sulphursenious acids. They farther agree in the analogy of their compounds with hydrogen, particularly of binoxide of hydrogen and bisulphide of hydrogen, both of which bleach, and are remarkable for their instability; and in the analogy of the oxide, sulphide, and telluride of ethyl, and of alcohol and mercaptan, which last is an alcohol with its oxygen replaced by sulphur. This class is connected with the next by manganese, of which manganic acid is isomorphous with sulphuric acid, and consequently manganese with sulphur.

II. *Magnesian Class.*—This class comprises magnesium, calcium, manganese, iron, cobalt, nickel, zinc, cadmium, copper, hydrogen, chromium, aluminum, glucinum, vanadium, zirconium, yttrium, thorinum. The protoxides of this class, including water, form analogous salts with acids. A hydrated acid, such as crystallized oxalic acid or the oxalate of water, corresponding with the oxalate of magnesia in the number of atoms of water with which it crystallizes, and the force with which the same number of atoms is retained at high temperatures; hydrated sulphuric acid (HO, SO_3+HO) with the sulphate of magnesia (MgO, SO_3+HO). The isomorphism of the salts of magnesia, zinc, cadmium, and the protoxides of manganese, iron, nickel, and cobalt, is perfect. Water (HO) and oxide of zinc (ZnO) have both been observed in thin regular six-sided prisms; but the isomorphism of these crystals has not yet been established by the measurement of the angles. Oxide of hydrogen has not, therefore, been shown to be isomorphous with these oxides, although it greatly resembles oxide of copper in its chemical relations. Lime is not so closely related as the other protoxides of this group, being allied to the following class. But its carbonate, both anhydrous and hydrated, its nitrate, and the chloride of calcium, assimilate with the corresponding compounds of the group; while to its sulphate or gypsum, CaO, SO_3+2HO, one parallel and isomorphous compound, at least, can be adduced, a sulphate of iron, FeO, SO_3+2HO (Mitscherlich), which is also sparingly soluble in water, like gypsum. Glucina is isomorphous with lime from the isomorphism of the minerals euclase and zoisite (Brooke).

The salts of the sesquioxide of chromium, of alumina, and glucina, are isomorphous with those of sesquioxide of iron ($Fe_2 O_3$), with which these oxides correspond in composition; and the salts of manganic and chromic acids are isomorphous, and agree with the sulphates. The vanadiates are believed to be isomorphous with the chromates. Zirconium is placed in this class, because its fluoride is isomorphous with that of aluminum and that of iron, and its oxide appears to have the same constitution as alumina; and yttrium and thorium, solely because their oxides, supposed to be protoxides, are classed among the earths.

III. *Barium Class.*—Barium, strontium, lead. The salts of their protoxides, baryta, strontia, and oxide of lead, are strictly isomorphous, and one of them at least, oxide of lead, is dimorphous, and assumes the form of lime, and the preceding class in the mineral plumbocalcite, a carbonate of lead and lime (Johnston). But certain carbonates of the second class are dimorphous, and enter into the present class, as the carbonate of lime in arragonite, carbonate of iron in junckerite, and carbonate of magnesia procured by evaporating its solution in carbonic acid water to dryness by the water-bath (G. Rose), which have all the common form of carbonate of strontia. Indeed, these two classes are very closely related.

IV. *Potassium Class.*—The fourth class consists of potassium, ammonium, sodium, silver. The term ammonium is applied to a hypothetical compound of one atom of nitrogen and four of hydrogen (NH_4), which is certainly, therefore, not an elementary body, and probably not even a metal, but which is conveniently assimilated in name to potassium, as these two bodies occupy the same place in the two great classes of potassa and ammonia salts, between which there is the most complete isomorphism. Potassium and ammonium themselves are, therefore, isomorphous. The sulphates of soda and silver are similiform, and hence also the metals sodium and silver; but their isomorphism with the preceding pair is not so clearly established. Soda replaces potassa in soda-alum, but the form of the crystal is the common regular octohedron; nitrate of potassa has also been observed in microscopic crystals, having the arragonitic form of nitrate of soda,[1] which is better evidence of isomorphism, although not beyond cavil, as the crystals were not measured. There are also grounds for believing that potassa replaces soda in equivalent quantities in the mineral chabasite, without change of form. The probable conclusion is, that potassa and soda are isomorphous, but that this relation is concealed by dimorphism, except in a very few of their salts.

This class is connected in an interesting way with the other classes through the second. The subsulphide of copper and the sulphide of silver appear to be isomorphous, (see *sulphide of silver*, under silver, in this work), although two atoms of copper are combined in the one sulphide, and one atom of silver in the other, with one atom of sulphur; their formulæ being—

$$Cu_2\,S \text{ and } Ag\,S.$$

Are then *two* atoms of copper isomorphous with *one* atom of silver? In the present state of our knowledge of isomorphism, it appears necessary to admit that they are.

The fourth class will thus stand apart from the second, which is represented by copper, and also from the other classes connected with the second, in so far as one atom of the present class is equivalent to two atoms of the other classes in the production of the same crystalline form. This discrepancy may be at once removed by halving the atomic weight of silver, and thus making both sulphides to contain two atoms of metal to one of sulphur. But the division of the equivalents of sodium, potassium, and ammonium, which would follow that of silver, and the consideration of potassa and soda as suboxides, are assumptions not to be lightly entertained.

It was inferred by M. Mosander, that lime with an atom of water is isomorphous with potassa and soda, because $CaO + HO$ appears to replace KO or NaO in mesotype, chabasite, and other minerals of the zeolite family. The isomorphism of natrolite and scolezite is so explained: $NaO, Al_2\,O_3, 2SiO_3, 2HO$ with $CaO, Al_2\,O_3, 2SiO_3, 3HO$. On the other hand, it is strongly argued by M. T. Scheerer, that one equivalent of magnesia is isomorphous with three equivalents of water, from the equality of the forms of cordierite and a new mineral aspasiolite, the first containing MgO, and the second $3HO$ in its place; and from a review of a considerable number of alumino-magnesian minerals. One equivalent of oxide of copper, however, is supposed to be replaced by two equivalents of water.[2]

V. *Chlorine Class.*—Chlorine, iodine, bromine, fluorine. These four elements form a well-defined natural family. The three first are isomorphous throughout their whole combinations—chlorides with bromides and iodides, chlorates with bromates and iodates, perchlorates with periodates, &c.; and such fluorides also as can be compared with chlorides appear to affect the same forms. The fluoride of calcium of apatite, $CaF, 3(3CaO, PO_5)$, is also replaced by the chloride of calcium. It is connected with the second class through perchloric acid; the perchlorates being strictly isomorphous with the permanganates. But the formulæ of these two acids are—

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[1] Frankenheim, in Poggendorff's *Annalen*, vol. xl. page 447. See also a paper by Professor Johnston on the received equivalents of potassa, soda, and silver; Phil. Mag. third series, vol. xii. p. 324.

[2] Poggendorff's *Annalen der Physik und Chemie*, t. lxviii. p. 319. Also, Millon and Reiset's Annuaire de Chimie, 1847, 8vo. Paris, pp. 52 and 234.

$$Cl\,O_7 \text{ and } Mn_2\,O_7,$$

one atom of chlorine replacing two atoms of manganese. Or, this class has the same isomorphous relation as the preceding class to the others: and such I shall assume to be its true relation. Although halving the atomic weight of chlorine, which would give two atoms of chlorine to perchloric acid, is not an improbable supposition, still it would lead to the same strange conclusion as follows the division of the equivalent of sodium,—namely, that chlorine enters into its other compounds, as well as into perchloric acid, always in the proportion of two atoms; for that element is never known to combine in a less proportion than is expressed by its presently received equivalent. Cyanogen ($C_2\,N$), although a compound body, has some claim to enter this class, as the cyanides have the same form as the chlorides.

VI. *Phosphorus Class.*—Nitrogen, phosphorus, arsenic, antimony, and bismuth; also composing a well-marked natural group, of which nitrogen and bismuth are the two extremes, and of which the analogous compounds exhibit isomorphism. These five elements all form gaseous compounds with three atoms of hydrogen; namely, ammonia, phosphuretted hydrogen, arseniettėd hydrogen, &c. The hydriodates of ammonia and of phosphuretted hydrogen are not, however, isomorphous. Arsenious acid and the oxide of antimony, both of which contain three atoms of oxygen to one of metal, are doubly isomorphous. Arsenious acid also is capable of replacing oxide of antimony in tartrate of antimony and potassa or tartar emetic, without change of form; and arsenic often substitutes antimony in its native sulphide. The native sulphide of bismuth ($Bi\,S_3$) is also isomorphous with the sulphide of antimony ($Sb\,S_3$). Nitrous acid (NO^3), which should correspond with arsenious acid and oxide of antimony, likewise acts occasionally as a base, as in the crystalline compound with sulphuric acid of the leaden chambers. The complete isomorphism of the arseniates and phosphates has already been noticed. But phosphoric acid forms two other classes of salts, the pyrophosphates and metaphosphates, to which arsenic acid supplies no parallels.

This class of elements is connected with the others by means of the following links:—Bisulphide of iron is usually cubic, or of the regular system; but it is dimorphous, and, in spirkise, it passes into another system, and has the form of arsenide of iron; $Fe\,S_2$, or rather $Fe_2\,S_4$, being isomorphous with $Fe_2\,As\,S_2$. Again, bisulphide of iron, in the pentagonal-dodecahedron of the regular system, is isomorphous with cobalt-glance, $Fe_2\,S_4$ with $Co_2\,As\,S_2$: so that one equivalent of arsenic appears to be isomorphous with 2S. This is also supported by the isomorphism of the sulphide of cadmium and sulphide of nickel ($Cd\,S$ and $Ni\,S$, or $Cd_2\,S_2$ and $Ni_2\,S_2$), with the arsenide of nickel ($Ni_2\,As$). Tellurium has also been observed in the same form as metallic arsenic and antimony. The phosphorus class approximates also to the chlorine class; nitrogen and chlorine both forming a powerful acid with five equivalents of oxygen, nitric acid, and chloric acid; but of the many nitrates and chlorates which can be compared, no two have proved isomorphous. Nor do the metaphosphates appear at all like the nitrates, although their formulæ correspond.

Nitrogen, it must be admitted, is but loosely attached to this class. It is greatly more negative than the other members of the class, approaching oxygen in that character, with which, indeed, nitrogen might be grouped, N being equivalent to 2O. For while phosphuretted hydrogen is the hydride of phosphorus, or has hydrogen for its negative and phosphorus for its positive constituent, ammonia is undoubtedly the nitride of hydrogen, or has nitrogen for its negative and hydrogen for its positive constituent. The one should be written PH_3, and the other H_3N—a difference in constitution which separates these bodies very widely. An important consequence of classing nitrogen with oxygen is, that, in the respective series of compounds of these elements, cyanogen becomes the analogue of carbonic oxide, C_2N being equivalent to CO, or rather C_2O_2.

VII. *Tin Class.* — Tin, titanium. Connected by the isomorphism of titanic acid (TiO_2) in rutile with peroxide of tin (SnO_2) in tin-stone. Titanium is connected with iron and the second class. Ilmenite and other varieties of titanic iron which have the crystalline form of the sesquioxide of that metal, — namely, that of specular iron, and also of corundum (alumina), — are mixtures of a sesquioxide of titanium (Ti_2O_3) with sesquioxide of iron (H. Rose).

VIII. *Gold Class.* — Gold, which is isomorphous with silver in the metallic state. Gold will thus be connected, through silver, with sodium and the fourth class.

IX. *Platinum Class.* — Platinum, iridium, osmium. From the isomorphism of their double chlorides. The double bichloride of tin and chloride of potassium crystallizes in regular octohedrons, like the double bichloride of platinum and potassium, and other double chlorides of this group; which, although not alone sufficient to establish an isomorphous relation between this class and the seventh, yet favours its existence (Dr. Clark). The alloy of osmium and iridium (IrOs) is isomorphous with the sulphide of cadmium (CdS) and sulphide of nickel (NiS) (Breithaupt).

X. *Tungsten Class.* — Tungsten, molybdenum, tantalum, niobium, and pelopium. From the isomorphism of the tungstates and molybdates, the salts of tungstic and molybdic acids, WO_3 and MoO_3. Tantalic acid is isomorphous with tungstic acid: tantalite (FeO, TaO_3) with wolfram (FeO, WO_3). So are molybdic and chromic acids, the tungstate of lime, tungstate of lead, molybdate of lead, and chromate of lead (in the least usual of its two forms), being all of the same form. This establishes a relation between molybdic, chromic, sulphuric, and other analogous acids (Johnston, Phil. Mag. 3d series, vol. xii. p. 387). Niobium and pelopium are introduced into this class as they replace tantalum in the tantalites of Bavaria.

XI. *Carbon Class.* — Carbon, boron, silicium. These elements are placed together, from a general resemblance which they exhibit without any precise relation. They are not known to be isomorphous among themselves, or with any other element. They are non-metallic, and form weak acids with oxygen, — the carbonic, consisting of two of oxygen and one of carbon, and the boric and silicic acids, which are generally viewed as composed of three of oxygen to one of boron and silicium. Silicic acid may, perhaps, replace alumina in some minerals, but this is uncertain.

Of the elements which have not been classed, no isomorphous relations are known. They are mercury, which in some of its chemical properties is analogous to silver, and in others to copper, cerium, didymium, lanthanum, lithium, rhodium, ruthenium, palladium, and uranium. Ruthenium, however, is believed to be isomorphous with rhodium, from the correspondence in composition of their double chlorides. Didymium and lanthanum are also probably isomorphous with cerium, as they appear to replace that metal in cerite.

According to the original law of Mitscherlich, that isomorphism depends upon equality in the number of atoms, and similarity in their arrangement, without reference to their nature, the elements themselves should all be isomorphous. Most of the metals crystallize in the simple forms of the cube or regular octohedron, which are not sufficient to establish this relation. But the isomorphism of a large proportion, if not the whole, of the elements may be inferred from the isomorphism of their analogous compounds. Thus, from the facts just adduced, it appears that the members of the following large class of elements are linked together from the isomorphism of one or more of their compounds. This large class may be subdivided into smaller classes, between the members of which isomorphism is of more frequent occurrence, and which are then to be viewed as isomorphous groups.

ISOMORPHOUS ELEMENTS.

1. Sulphur
Selenium
Tellurium

2. Magnesium
Calcium
Manganese
Iron
Cobalt
Nickel
Zinc
Cadmium
Copper
Chromium
Aluminum
Glucinum
Vanadium
Zirconium

3. Barium
Strontium
Lead

4. Tin
Titanium

5. Platinum
Iridium
Osmium

6. Tungsten
Molybdenum
Tantalum

With two atoms of the preceding elements.

7. Sodium
Silver
Gold
Potassium
Ammonium

Chlorine
Iodine
Bromine
Fluorine
Cyanogen

9. Phosphorus
Arsenic
Antimony
Bismuth

The tendency of discovery is to bring all the elements into one class, either as isomorphous atom to atom, or with the relation to the others which sodium, chlorine, and arsenic exhibit.

But must not isomorphism be implicitly relied upon in estimating atomic weights, and the alterations which it suggests be adopted without hesitation in every case? Chemists have always been most anxious to possess a simple physical character by which atoms might be recognised; and equality of volume in the gaseous state, equality of specific heat, and similarity in crystalline form, have all in their turn been upheld as affording a certain criterion. The indications of isomorphism certainly accord much better than those of the other two criteria with views of the constitution of bodies derived from considerations purely chemical, and are indeed invaluable in establishing analogy of composition in a class of bodies, by supplying a precise character which can be expressed in numbers, instead of that general and ill-defined resemblance between allied bodies, which chemists perceived by an acquired tact rather than by any rule, and which was heretofore their only guide in classification. Admitting that isomorphism is a certain proof of similarity of atomic constitution within a class of elements and their compounds, it may still be doubted whether the relation of the atom to crystalline form is the same without modification throughout the whole series of the elements, or whether all atoms agree exactly in this or any other physical character.

Crystalline form and the isomorphous relation may prove not to be a reflection of atomic constitution, or immediately and necessarily connected with it, but to arise from some secondary property of bodies, such as their relation to heat; in which a simple atom may occasionally resemble a compound body, as we find sulphur isomorphous in one of its forms with bisulphate of potassa; while we find another simple atom, potassium, isomorphous through a long series of compounds with the group of five atoms which constitute ammonium. The occurrence of dimorphism also, both in simple and compound bodies, gives to crystalline form a less fundamental character.

Is it probable that sulphur and carbonate of lime could be made to appear in sets of crystals which are wholly unlike, merely by a slight change of temperature, if form were the consequence of an invariable atomic constitution? Crystalline form, then, may possibly depend upon some at present unknown property of bodies, which may have a frequent and general, but certainly not an invariable relation to their atomic constitution. There may be nothing truly inconsistent with the principles of isomorphism in one atom of a certain class of elements having the same crystallographic value as two atoms of another class, the relation which has been assumed to exist between the sodium, chlorine, and phosphorus classes, and the others, particularly when the classes stand apart, and differ in their properties from all the others, as those of sodium and chlorine do.

SECTION V.—ALLATROPY.

Many solid, and a few liquid bodies admit of a variation of properties, and may present different appearances at the same temperature.

Dimorphism, or the assumption of two incompatible crystalline forms by the same body, in different circumstances, has already been noticed as occurring with sulphur, carbon, carbonates of lime and lead, bisulphate of potassa, and chromate of lead. It is also observed in the biphosphate of soda, and in a considerable number of minerals. The sulphate of nickel (NiO, SO_3+7HO) is *trimorphous;* the other salts of similar composition, such as sulphate of magnesia and sulphate of zinc, have been found in two only of these forms. Dimorphous crystals may differ in density, the densities of calc-spar and arragonite, the forms of carbonate of lime being 2.719 and 2.949, and indeed all resemblance in properties between the crystals may be lost, as in diamond and graphite, the two forms of carbon. The particular form assumed by sulphur and carbonate of lime, which may be made to crystallize in either of their forms at will, is found to depend upon the degree of temperature at which the solid is produced; carbonate of lime being precipitated, on adding chloride of calcium to carbonate of ammonia, in a powder, of which the grains have the form of calc-spar or of arragonite, according as the temperature of the solution is 50° or 150° (G. Rose, Phil. Mag. 3d series, vol. xii. p. 465). A large crystal of arragonite, when heated by a spirit-lamp, decrepitates, and falls into a powder composed of grains of calc-spar. Native carbonate of iron is isodimorphous with carbonate of lime; as spathic iron its specific gravity is 3.872, as junckerite 3.815. The crystals of sulphur produced at the higher of two temperatures become opaque when kept for some days in the air, and pass spontaneously into the other form; while the crystals produced at the lower temperature are disintegrated and changed into the other form by a moderate heat. These observations are important, as establishing a relation between dimorphism and solidification at different temperatures.

A considerable variation of properties is likewise often observable in a solid which is not crystalline, or of which the crystalline form is indeterminate. This fact has been designated *allatropy* by Berzelius (from ἀλλοτροπος, of a different nature): dimorphism, or diversity in crystalline form, is, therefore, a particular case of allatropy. Sulphide of mercury obtained by precipitating corrosive sublimate by hydrosulphuric acid, is black; but the same body, when sublimed by heat, or produced by agitating mercury in a solution of the persulphide of potassium, forms cinnabar, of which the powder is the red pigment vermilion; while vermilion itself, if heated till sulphur begins to sublime from it, and then suddenly thrown into cold water, becomes black; although, if allowed to cool slowly, it remains red. Yet it is of the same composition exactly in the black and red states. The iodide of mercury newly sublimed is of a lively yellow colour, and may remain so for a long time; but it generally begins to pass into a fine scarlet on cooling, and may be made to undergo this change of colour in an instant by strongly pressing it: these, however, are two different crystalline forms. The precipitated sulphide of antimony may be deprived of the water it contains, at the melting point of tin, without losing its peculiar orange colour; but, when heated a little above that temperature, it shrinks, and assumes the black colour and metallic lustre of the native sulphide, without any loss of weight. Again, the black sulphide, when heated strongly and thrown into water, loses its metallic lustre, and acquires a good deal of the appearance of the precipitated sulphide. Chromate of lead, which is usually yellow, if fused and thrown into cold water, gives a red powder. The nitrates of lead are sometimes white, and sometimes yellow; and crystals of sulphate of manganese are often deposited from the same solution, some of which are pink, and others colourless, although identical in composition.

Such differences of colour are permanent, and not to be confounded with changes which are peculiar to certain temperatures: thus oxide of zinc is of a lemon-yellow colour, when strongly heated, but milk-white at a low temperature; the oxide of mercury is much redder at a high than at a low temperature, and bichromate of potassa, which is naturally red, becomes almost black when fused by heat. Even bodies in the gaseous state are liable to transient changes of this kind, the brown nitrous fumes being nearly colourless below zero, and on the other hand deepening greatly in colour at a high temperature.

The condition of *glass* is a remarkable modification of the solid form assumed by many bodies. Matter in this state is not crystallized, and on breaking, presents curved and not plain surfaces, or its fracture, in mineralogical language, is *conchoidal,* and not *sparry.* The indisposition to crystallize, which causes solidification in the form of glass, is more remarkable in some bodies, such as phosphoric and boracic acids, and their compounds, than in others. The biphosphate and binarseniate of soda have the closest resemblance in properties, yet when both are fused by a lamp, the first solidifies on cooling into a transparent colourless glass, and the second into a white opake mass composed of interlaced crystalline fibres. The phosphate at the same time discharges sensibly less heat than the arseniate in solidifying, retaining probably a portion of its heat of fluidity, or latent heat in a state of combination, while a glass. None of the compounds of silicic acid and a single base, such as soda or lime, or simple silicate, becomes a glass on cooling from a state of fusion, with the exception of the silicate of lead containing a great excess of oxide: they all crystallize. But a *mixture* of the same silicates, when fused, exhibits a peculiar viscosity or tenacity, appears to have lost the faculty of crystallizing, and constantly forms a glass. The varieties of glass in common use are all such mixtures of silicates. Glass is sometimes devitrified when kept soft by heat for a long time, owing to the separation of the silicates from each other, and their crystallization; and the less mixed glasses are known to be most liable to this change. It is probable that all bodies differ, when in the vitreous and in the crystalline form, in the proportion of combined heat which they possess, as has been observed of melted sugar (page 61) in these two conditions.

Arsenious acid, when fused or newly sublimed, appears as a transparent glass of a light yellow tint; but left to itself, it slowly becomes opake and milk white, the change commencing at the surface and advancing to the centre, and often requiring years to complete it, in a considerable mass. The arsenious acid is no longer vitreous, being changed into a multitude of little crystals, whence results its opacity; and it has altered slightly at the same time in density and in solubility. But the passage from the vitreous to the crystalline state may take place instantaneously, and give rise to an interesting phenomenon observed by H. Rose. The vitreous arsenious acid seems to dissolve in dilute and boiling hydrochloric acid without change, but the solution on cooling deposits crystals which are of the opake acid, and a flash of light, which may be perceived in the dark, is emitted in the formation of each crystal. This phenomenon depends upon and indicates the transition, for it does not occur when arsenious acid already opaque is substituted for vitreous acid, and dissolved and allowed to crystallize in the same manner.

A still greater change than those described, is induced upon certain bodies by exposure to a high temperature, without any corresponding change in their composition. Several metallic peroxides, such as alumina, sesquioxide of chromium and binoxide of tin, cease to be soluble in acids after being heated to redness. The same is true of a variety of salts, such as many phosphates, tungstates, antimoniates, and silicates. Many of these bodies contain water in combination, when most readily dissolved by acids, which constituent is dissipated at a high temperature, but in general before the loss of solubility occurs, so that the contained water alone is not the cause of the solubility. Berzelius remarked an appearance often observable when such bodies are under the influence of heat, and in the act of passing from the soluble to the insoluble state. They suddenly glow or become luminous, rising in temperature above the containing vessel, from a discharge of heat. The rare mineral gadolinite, which is a silicate of yttria, affords a beautiful example of this change. When heated it appears to burn, emits light, and becomes yellow, but undergoes no change in weight. Fluorspar, and many other crystalline substances, exhibit a feeble phosphorescence when heated, which has no relation to this change, and is to be distinguished from it.

The circumstance most certain respecting this change in bodies, which affects so deeply their chemical properties, is that the bodies do not contain a quantity of heat, after the change, which they must have possessed before its occurrence in a combined or latent form. No ponderable constituent is lost, but there is this loss of heat. A change of arrangement of the particles, it is true, must occur at the same time in some of these bodies, such as is observed when sulphite of soda is converted by heat into a mixture of sulphate of soda and sulphuret of sodium, without change of weight; but it would be difficult to apply an explanation of this nature to oxides, such as alumina and binoxide of tin, which contain only two constituents, and still more so to an element such as carbon. The loss of heat observed will afford all the explanation necessary, if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may justly be viewed as the higher *caloride*, and the body in question may have different proportions of this as well as of any other constituent. But it is to be regretted that our knowledge respecting heat as a constituent of bodies is extremely limited; the definite proportion in which it enters into ice and other solids in melting, and into steam and vapours, has been studied, and also the proportion emitted during the combustion of many bodies, which has likewise proved to be definite. But the influence which its addition or subtraction may have on the chemical properties of a body is at present entirely matter of conjecture. The phenomena under consideration seem to require the admission of heat as a true constituent which can modify the properties of bodies very considerably; otherwise a great physical law must be abandoned, namely, that "no change of properties can occur without a change of composition." But if heat be once admitted as a chemical constituent of bodies, then a solution of the present difficulties may be looked for, for nothing is more certain than that "a change in composition will account for any change in properties." Heat thus combined in definite proportions with bodies, and viewed as a constituent, must not be confounded with the specific heat of the same bodies, or their capacity for sensible heat, which may have no relation to their combined heat.

SECTION VI. — ISOMERISM.

In such changes of properties as have already been described, the individuality of the body is never lost. But numerous instances have presented themselves of two or more bodies possessing the same composition, which are unquestionably different substances, and not mutually convertible into each other. Different bodies thus agreeing in composition, but differing in properties, are said to be *isomeric*, (from ἰσος, equal, and μερος, part), and their relation is termed *isomerism*. The discovery of such bodies excited much interest, and they have received a considerable share of the attention of chemists. But the result of a careful study of the bodies associated by similarity of composition, though differing in properties, has been upon the whole unfavourable to the doctrine of isomerism. Isomeric bodies have in general been proved by the progress of discovery to agree in the relative proportion of their constituents only, and to differ either in the aggregate number of the atoms composing them, or in the mode of arrangement of these atoms; and although new cases of isomerism are constantly arising, others are removed as they come to admit of explanation. This is what was to be expected, for isomerism in the abstract is improbable; a difference in properties between bodies, without a difference in their composition, appearing to be an effect without a sufficient cause. Hence, the term isomerism is now generally employed in a limited sense, to indicate simply the identity in composition of two or more bodies as expressed in the proportion of their constituents in 100 parts. Several classes of such isomeric bodies may be formed.

The members of the most numerous class of isomeric bodies differ in atomic weight. Thus we know at present three gases, three or four liquids, and as many solids, which all consist exactly of carbon and hydrogen, in the proportion of one atom to one atom, or, in weight, of 86 parts of carbon and 14 of hydrogen, very nearly. These agree in ultimate composition, but differ completely in every other respect. But a representation of their chemical constitution explains at once the cause of the differences they present, as is obvious in the following formulæ of four well characterized members of this isomeric group: —

	Equivalents and combining measure.
Olefiant gas	C_4H_4 or 4 volumes.
Gas from oil	C_8H_8 or 4 volumes.
Naphthene	$C_{16}H_{16}$ or 4 volumes.
Cetene	$C_{32}H_{32}$ or 4 volumes.

It thus appears that the atom of cetene contains twice as many atoms of carbon and hydrogen as the atom of naphthene, four times as many as the atom of the gas from oil, and eight times as many as the atom of olefiant gas; while as the atom of all these bodies affords the same measure of vapour, or four volumes, they must differ as much in density as they do in the number of their constituent atoms. It is not surprising, therefore, that they all possess different and peculiar properties. Several groups of bodies might be selected from the Table at page 130, which have a similar relation to each other, the number of their atoms being different, although their relative proportion is the same: such as —

Oil of lemons	$C_{10}H_8$
Oil of turpentine	$C_{20}H_{16}$
and,	
Naphthaline	$C_{20}H_8$
Paranaphthaline	$C_{30}H_{12}$

A still more remarkable case is presented by alcohol and the ether from wood-spirit, in which there is identity of condensation as well as of composition, with different equivalents. The vapours of these two liquids have in fact the same specific gravity, and contain, under equal volumes, equal quantities of carbon, hydrogen, and oxygen. But we know that they are of a different type, alcohol being the hydrated oxide of ethyl, and ether of wood-spirit the oxide of methyl, so that their constitution and rational formulæ are quite different: —

Alcohol	C_4H_5O+HO.
Ether of wood-spirit	C_2H_3O.

In another class of isomeric bodies, the atomic weight may be equal, as well as the elementary composition. A pair belonging to this class are known, which coincide besides in the specific gravity of their vapours. The composition and atom of both the formiate of the oxide of ethyl (formic ether) and the acetate of oxide of methyl, may be represented by $C_6H_5O_4$: the density of both their vapours is 2574: and what is very remarkable, these bodies in their ordinary liquid state almost coincide in properties, the density of formic ether being 0·916, and that of the acetate of methylene 0·919, (density of water being =1.000), while the first boils at 133°, and the last at 136·4°. But when acted on by alkalies, their products are entirely different, the one affording formic acid and alcohol, and the other acetic acid and wood-spirit. Each of the isomeric bodies in question contains, indeed, two different binary compounds, and their constitution is truly represented by different formulæ: —

Formiate of oxide of ethyl........................ $C_4H_5O + C_2HO_3$
Acetate of oxide of methyl........................ $C_2H_3O + C_4H_3O_3$

in which the same atoms are seen to be very differently arranged. The term *metameric* has been applied to bodies so related.

The last class of isomeric bodies are of the same atomic weights, but their constitution or molecular arrangement being unknown, their isomerism cannot at present be explained. It can scarcely be doubted, however, that their molecular arrangement is really different.

One pair of such isomeric bodies will illustrate the coincidences observed not at all unfrequently among organic substances. The racemic and tartaric acids, of which the composition is the same, exhibit a similarity of properties, and a parallelism in their chemical characters, that are truly astonishing. These acids are found together in the grape of the Upper Rhine. They differ considerably in solubility, the racemic being the least soluble, so that they may be separated from each other by crystallization; and the racemic acid contains an atom of water of crystallization, which is not found in the crystals of tartaric acid. They form salts which correspond very closely in their solubility and other properties. The bitartrate and biracemate of potassa are both sparingly soluble salts: the tartrates and racemates of lime, lead, and barytes, are all alike insoluble. Both acids form a double salt with soda and ammonia, which is an unusual kind of combination. But what is most surprising, crystals of these double salts not only coincide in the proportion of their water and other constituents, and in the composition of their acids, but also in external form, having been observed by Mitscherlich to be isomorphous. A nearer approach to identity could scarcely be conceived than is exhibited by these salts, which are, indeed, the same both in form and composition. The crystallized acids are both modified in an unusual manner by heat, and form three classes of salts, as phosphoric acid does. The formulæ of both acids in their ordinary class of salts is $C_8H_4O_{10}$ + two atoms of base (Fremy); but by no treatment can the one acid be transmuted into the other. Lastly, every organic acid produces a new acid by destructive distillation, which is peculiar to it, and is termed its pyr-acid. Now racemic and tartaric acid, when destroyed by heat, agree in giving birth to one and the same pyr-acid.

The allatropy of elements has been supposed to throw light upon the multiplication of series of compounds arising from one radical, and the isomerism of certain compounds. Fused sulphur passes through several allatropic conditions as its temperature is raised, in which it is imagined that the equivalent of the element may be doubled, tripled, and even quadrupled by a coalition of so many single atoms and the formation of compound atoms, which are distinguished as α sulphur, β sulphur, δ sulphur, γ sulphur, &c. In the different series of the oxygen acids of sulphur, containing one, two, three, and four equivalents of sulphur, the different allatropic varieties of sulphur are imagined to exist. Silicium in its combustible and incombustible allatropic conditions may thus give rise to different silicic acids, and allatropic borons and tungstens to the isomeric boric and tungstic acids.

SECTION VII. — ARRANGEMENT OF THE ELEMENTS IN COMPOUNDS.

The names of some compounds imply that they contain other compounds, and indicate a certain atomic constitution, while the names of other compounds express no particular arrangement of their constituent atoms, but leave it to be inferred that the atoms are all directly combined together. Thus sulphate of soda implies the continued existence of sulphuric acid and soda in the salt, while nitric acid, or binoxide of hydrogen, supposes no partition of the compound to which it is applied. But it is to be remembered that the original framers of the nomenclature were guided more by facilities of an etymological nature, in constructing such terms, than by views of the constitution of compounds.

Of a binary compound containing single atoms of its constituents, there cannot be two modes of representing the constitution; but where one of the constituents is present in the proportion of two or more atoms, several hypotheses can always be formed of their mode of aggregation. In a series of binary combinations of the same elements, such as that of nitrogen and oxygen, NO_1, NO_2, NO_3, NO_4, NO_5, the simplest view has generally been taken, namely, that it is the elements themselves which unite. But in particular cases the chemist is often involuntarily led into another opinion. Thus binoxide of nitrogen is so often a product of the decomposition of nitric acid, that the acid appears more like a compound of that oxide of nitrogen with oxygen, than a compound of nitrogen itself with oxygen. When the binoxide of hydrogen was first discovered by Thénard, he was led by the whole train of its properties to view it as a compound of water and oxygen, into which it is resolved with so much facility, and to name it accordingly *oxygenated water*, which it may be, and not a direct combination of hydrogen and oxygen; or its formula be $HO+O$, and not HO_2. The periodide of potassium, and the other analogous compounds obtained by dissolving iodine in metallic iodides, were first termed *ioduretted iodides* from similar considerations, and the hyposulphites, obtained by dissolving sulphur in sulphites, *sulphuretted sulphites*. It may be doubted whether chemists would return with advantage to any of these expressions, the views of composition which they indicate being uncertain, and not offering a sufficient inducement to depart from the more systematic designations. The binoxide of hydrogen, for instance, may be easily resolved into water and oxygen, not because water pre-exists in it, but because water is a compound of great stability, and is formed when binoxide of hydrogen is decomposed. Nitric acid, also, is as likely to be a compound of quadoxide of nitrogen with an additional atom of oxygen, as of binoxide of nitrogen with three atoms of the same element.

Certain compound bodies, however, have been observed to act the part of a simple body in combination, and can be traced through a series of compounds. The following substances, for instance, may be represented with considerable probability as compounds of carbonic oxide, as in the formulæ:—

CO, carbonic oxide.
$CO+O$, carbonic acid.
$CO+Cl$, chloroxicarbonic acid.
$2CO+O$, oxalic acid.

Carbonic oxide is said to be the *radical* of this series, a name applied to any compound which is *capable of combining with simple bodies*, as carbonic oxide appears to do with oxygen and chlorine in these compounds. Messrs. Liebig and Wöhler first proved by decisive experiments that such a radical exists in the benzoic combinations, which may be represented thus:—

$C_{14}H_5O_2+O$, benzoic acid.
$C_{14}H_5O_2+H$, essential oil of bitter almonds.
$C_{14}H_5O_2+Cl$, chloride of benzoyl, &c.

Cyanogen was the first recognised member of the class of compound radicals, of which the number known to chemists is constantly increasing, and which appear to pervade the whole compounds of organic chemistry. In combining with simple bodies, radicals act the part of other simple bodies, such as metals, chlorine, oxygen, &c., which they replace in compounds.

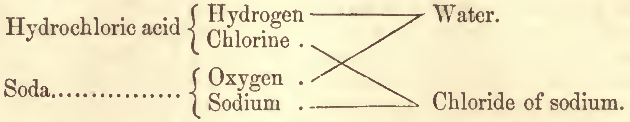
With the elements themselves compound radicals may be divided into two great classes:—

The *Basyl* class, consisting of metals the oxides of which are bases, hydrogen, the corresponding compound radicals, ammonium, ethyl, &c. These are electropositive bodies.

The *salt-radical* class—chlorine, sulphur, oxygen, &c., with cyanogen, and other compound radicals which combine with metals and other members of the former class, and form salts or compounds partaking of the saline character. Such radicals are also termed *salogens;* they are electro-positive.

Constitution of salts.—Of the supposed combinations of binary compounds with binary compounds, the most numerous and important class are salts. Sulphate of soda is commonly viewed as a direct combination of sulphuric acid and soda, each preserving its proper nature in the compound; and so are all similar compounds of an acid oxide with a basic oxide. An oxygen acid is allowed to exist in them, and they are particularly distinguished as "oxygen-acid salts." But an opinion was promulgated long ago by Davy, that these salts might be constituted on the plan of the binary compounds of the former class, and their hydrated acids on the plan of a hydrogen acid; a view which is supported by many analogies, and has latterly had a preference given to it by some of our leading chemical authorities. It is, therefore, deserving of serious consideration.

One class of acids, the hydrogen acids, and the salts which they produce with alkalies, are unquestionably binary compounds, and were assumed by Davy as the types of acids and salts in general. Hydrochloric acid is composed of two elements, chlorine and hydrogen, and with soda it forms water and chloride of sodium, thus:—



the hydrogen of the acid being replaced by sodium in the salt formed. Hydrocyanic is another hydrogen acid, of which cyanide of sodium is a salt. In general terms, a *radical* (which may be either simple or compound, like chlorine or cyanogen) forms an *acid* with hydrogen, and a *salt* with sodium or any other metal.

Hydrated sulphuric acid, which consists of sulphuric acid and an atom of water, $HO+SO_3$, is represented as a hydrogen acid by transferring the oxygen of the water to the sulphuric acid to form a new radical, SO_4, which is supposed to be in direct combination with the remaining atom of hydrogen, as $H+SO_4$. In sulphate of soda, the oxygen of the soda is in the same manner transferred to the acid, or the formula of the salt is changed from $NaO+SO_3$ to $Na+SO_4$. To SO_4, the salt-radical of sulphates, the name *sulphion* has been applied, from the circumstance that, in the voltaic decomposition of a sulphate, SO_4, travels to the positive pole, and the metal or hydrogen to the negative pole. Its compounds, or the sulphates, become *sulphionides.* The hydrated acid and its soda salt are thus named and denoted on the two views of their constitution—

I. ON THE ACID THEORY:

Hydrated sulphuric acid, sulphate of oxide of hydrogen, or hydric sulphate	$HO+SO_3$
Sulphate of soda, sulphate of oxide of sodium, or soda sulphate	$NaO+SO_3$

II. ON THE SALT-RADICAL THEORY:

Sulphionide of hydrogen	$H+SO_4$
Sulphionide of sodium	$Na+SO_4$

which last formulæ are strictly comparable with those of an admitted hydrogen acid and its salt, such as—

Hydrochloric acid or chloride of hydrogen	$H+Cl$
Chloride of sodium	$Na+Cl$

or as—

Hydrocyanic acid or cyanide of hydrogen	$H+C_2N$
Cyanide of sodium	$Na+C_2N$

which thus appear compounds of three different radicals, chlorine (Cl), cyanogen (C_2N), and sulphion (SO_4), with the same elementary bodies, hydrogen and sodium. Sulphion is known only in combination, and has not been obtained in a separate state like chlorine and cyanogen. The body, sulphuric acid, SO_3, which may be separated from some sulphates, and can exist by itself, is looked upon as a product of the decomposition of these salts, and not to pre-exist in them, so that a secondary character is assigned to it.

Hydrated nitric acid, or aqua fortis, becomes a hydrogen acid by the creation of a nitrate radical, nitration. It is the nitrationide of hydrogen instead of the nitrate of water—

$$H + NO_6, \text{ instead of } HO + NO_5.$$

The nitrate of potassa becomes the nitrationide of potassium, and so of all other nitrates.

It is evident that the same view is applicable to hydrated oxygen acids in general, which may be made hydrogen acids, by assuming the existence of a new salt-radical for each, containing an atom more of oxygen than the oxygen acid itself, and capable of combining directly with hydrogen and the metals. The class of oxygen acid salts is thus abolished, and they become binary compounds like the chlorides and cyanides. Even oxygen acids themselves can no longer be recognized. It is not sulphuric acid (SO_3), but what was former viewed as its compound with water, that is the acid, and it is a hydrogen acid. The properties which characterize acids are undoubtedly only observed in the hydrates of the oxygen acids. Thus the anhydrous sulphuric acid does not redden litmus, and exhibits a disposition to combine with salts, such as chloride of potassium and sulphate of potassa, rather than with bases. The liquid carbonic acid has little affinity for water, does not combine directly with lime, but dissolves in alcohol, ether, and essential oils, like certain neutral bodies. It is only when associated with water that the bodies referred to exhibit acid properties, and then hydrogen acids may be produced.

On this view, it is obvious that the acid and salt are really bodies of the same constitution, hydrochloric acid being the chloride of hydrogen, as common salt is the chloride of sodium, and sulphuric acid and sulphate of soda being the sulphionides of hydrogen and of sodium. The acid reaction and sour taste are not peculiar to the hydrogen compound, and do not separate it from the others; the chloride, sulphionide, and nitrationide of copper being nearly as acid and corrosive as the chloride, sulphionide, and nitrationide of hydrogen, and clearly bodies of the same character and composition: they are all equally salts in constitution. The term "acid" is not absolutely required for any class of bodies included in the theory, and might, therefore, be dropped, if it were not that an inconvenience would be felt in having no common name for such bodies as anhydrous sulphuric acid SO_3, anhydrous nitric acid NO_5, sulphurous acid SO_2, carbonic acid CO_2, &c. To these substances, which first bore the name, it should now be confined. In considering the generation of salts, three orders of bodies would be admitted, as in the following tabular exposition of a few examples:—

I.	II.	III.
The Acid.	The Salt-radical.	The Salt.
SO_3	SO_4	$SO_4 + H$ or a metal.
NO_5	NO_6	$NO_6 + H$ or a metal.
	NC_2	$NC_2 + H$ or a metal.
	Cl	$Cl + H$ or a metal.

The first term of the series, or "the acid," is wanting in the last two examples; and that is the peculiarity of those bodies which constituted the original class of hydrogen acids and their salts: while, to the old class of oxygen acid salts, both an acid and a salt-radical can be assigned, as in the first two examples.

The peculiar advantages of the salt-radical theory are—

First: That, instead of two, it makes but one great class of salts, assimilating in constitution bodies which certainly resemble each other in properties. Chloride of sodium and sulphate of soda are both neutral, and possess a common character, which is that of a soda salt; but they are separated widely from each other on the view of their constitution which is expressed in their names.

Secondly: It accounts for a remarkable law which is observed in the construction of salts; namely, that bases always combine with as many atoms of acid as they themselves contain of oxygen; a protoxide, which contains one atom of oxygen, combining and forming a neutral salt with one atom of an oxygen acid; while an oxide which contains two atoms of oxygen to one of metal, like binoxide of palladium, forms a neutral salt with two atoms of acid; and an oxide of three atoms of oxygen to two of metal, like sesquioxide of iron, forms a neutral salt with three atoms of acid. The acid and oxygen are thus always together in the exact proportion to form the salt-radical, there being always an atom of oxygen for every atom of acid in the salt. This will appear more distinctly in the following formulæ, which exhibit the composition of the neutral sulphates of a metal in four different states of oxidation, an atom of metal being represented by R:—

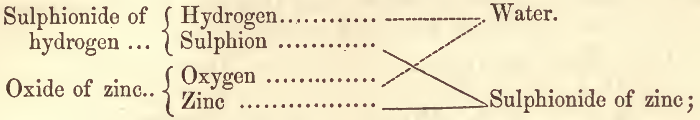
FORMULÆ OF NEUTRAL SULPHATES.

I. As consisting of Oxide and Acid.	II. As consisting of Metal and Salt-radical.	
$RO+SO_3$	$R+SO_4$	as in sulphate of soda.
R_2O+SO_3	R_2+SO_4	as in sulphate of suboxide of mercury.
RO_2+2SO_3	$R+2SO_4$	as in sulphate of binoxide of palladium.
$R_2O_3+3SO_3$	R_2+3SO_4	as in sulphate of sesquioxide of iron.

The acid is seen in the first column to be always in the proper proportion to form a sulphionide of the metal in the second column; and these sulphionides correspond exactly with known chlorides, such as RCl, R_2Cl, RCl_2, R_2Cl_3.

Thirdly: It offers a more simple and philosophical explanation of the action of certain metals upon acid solutions, and of the decomposition of such solutions in other circumstances. Thus when zinc is introduced into hydrochloric acid (chloride of hydrogen), it is allowed on both views, that the metal simply displaces the hydrogen which is evolved, and that chloride of zinc is formed in the place of chloride of hydrogen. In the same way, when zinc is introduced into diluted sulphuric acid, which contains the sulphionide of hydrogen on the binary theory, hydrogen is simply displaced and evolved as before, and the sulphionide of zinc is formed in the place of the sulphionide of hydrogen. The metal in question appears to be incapable of decomposing pure water by displacing its hydrogen at the temperature of the air; but this fact does not interfere with the preceding explanation, as zinc may have a greater affinity for sulphion than for oxygen, and, therefore, be capable of decomposing the sulphionide, but not the oxide of hydrogen. If the acid solution, however, contains sulphate of water, as it does on the old view, then zinc does and does not decompose water; decomposing it when in combination, but not when free. It becomes necessary to assume that the presence of the acid enhances the affinity of the metal for the oxygen of the water, in a manner which cannot be clearly explained; for the solubility of oxide of zinc in the acid, to which the influence of the acid is often ascribed, accounts for the continuance of the action, by providing for the removal of the oxide, rather than for its first commencement. The phenomena of the decomposition of an acid solution in the voltaic circle, are also most simply explained on the salt-radical theory. Oxide of hydrogen and sulphionide of hydrogen, are both binary "electrolytes," which are decomposed in the voltaic circle in the same manner, although not with equal facility; the common element, hydrogen, proceeding from both to the negative electrode, and oxygen in the one case and sulphion in the other to the positive electrode. The sulphion finds water there, and resolves itself into sulphionide of hydrogen and free oxygen. The decomposition of the sulphionide of sodium or any other salt may be explained in the same simple manner; while on the other view, it must be assumed that a simultaneous transference between the electrodes of acid and alkali with the oxygen and hydrogen of water takes place; and the effect of the acid in promoting the decomposition of the water remains unaccounted for.

When a metallic oxide is dissolved in an acid solution, as oxide of zinc in diluted sulphuric acid, the reaction which occurs is thus explained on the binary theory:



as in the reaction between the same oxide and hydrochloric acid (page 156).

The chief objections to the salt-radical theory, are—

First: The creation of so many hypothetical radicals; namely, one for every class of oxygen-acid salts. But it is to be remembered that the great proportion of oxygen acids, such as acetic, oxalic, &c. are equally of an ideal character, and cannot be exhibited in a separate state.

Secondly: The peculiarities of the salts of phosphoric acid which are supposed to be inimical to the new view. That acid forms three different and independent classes of salts, containing respectively one, two, and three, equivalents of base to one of acid. On the binary theory, these three classes of salts must contain three different salt-radicals, combined respectively with one, two, and three equivalents of hydrogen or metal. The three phosphates of water and the corresponding phosphionides of hydrogen would be represented as follows:—

I.	II.	III.
$HO+PO_5$	$2HO+PO_5$	$3HO+PO_5$
$H+PO_6$	$2H+PO_7$	$3H+PO_8$

Such salt-radicals and such compounds with hydrogen startle us, from their novelty, but it may be questioned whether they are really more singular than the anormal classes of phosphates, containing several equivalents of base, for which they are substituted, but which we have been more accustomed to contemplate. All the salt-radicals known in a separate state, such as chlorine and cyanogen, combine with one equivalent only of hydrogen, or are monobasylous, but it would be unfair to assume in the present imperfect state of our knowledge that other salt-radicals may not exist, capable of combining with two or three equivalents of hydrogen, as the phosphate-radicals are supposed to do. The existence of at least one such radical is highly probable, as will afterwards appear.

In conclusion, it may be stated that neither view of the constitution of the oxygen-acid salts, (which alone are affected by this discussion), rests on demonstrative evidence; they are both hypotheses, and are both capable of explaining all the phenomena of the salts. But to whichever of them a speculative preference is given, we can scarcely avoid using the language of the acid theory, in the present state of chemical science.

[Additional objections may be urged against the salt-radical theory:

As long as it is applied to salts constituted according to the law that "bases always combine with as many atoms of acid as they themselves contain of oxygen," the subject is without difficulty, but when it is applied to anhydrous compounds containing more than one equivalent of acid, it fails, or necessitates the creation of as many hypothetical salt-radicals as there are examples of this kind. Thus, the anhydrous sulphates of potassa and soda, the chromates, &c. are not mere combinations of one equivalent of the base with one and more equivalents of the acid, but become compounds of a metal with a greater number of salt-radicals. The neutral chromate of potassa, KO, CrO_3, is on the salt-radical theory; K, CrO_4, the bichromate; $KO, 2CrO_3$, is K, Cr_2O_7; and the terchromate, $KO, 3CrO_3$, is K, Cr_3O_{10}; or potassium combined with three different and new substances, each requiring a new and distinctive name. Moreover, the theory is involved in the same difficulty when the attempt is made to apply it to those salts which are exceptions to the above law, or in which the number of atoms of oxygen in the base does not correspond with the number of atoms of acid. The following example may be taken from the salts of tartaric acid, which, considered as bibasic, has the formula $C_8H_4O_{10}$, for which the conventional symbol $\bar{T}$ may be substituted, and we shall then have four of the salts represented below, on the old and new views of their constitution:

$KO, HO.\ \bar{T}=K, H.\ \bar{T}O_2$,	Cream of tartar.
$KO, NaO.\ \bar{T}=K, Na.\ \bar{T}O_2$	Rochelle salt.
$KO, Fe_2O_3.\ \bar{T}=K, Fe_2.\ \bar{T}O_4$	Tartarized iron.
$KO, SbO_3.\ \bar{T}=K, Sb.\ \bar{T}O_4$	Tartar emetic.

In the first two formulæ the elements are readily transposed to suit either view; but in the two latter a new hypothetical salt-radical appears, endowed with new powers, viz. the capability of combining respectively with two atoms of metallic-radical K, Sb, and with three atoms of radical K, Fe_2.

This theory explains very readily the reaction which takes place when water is decomposed under the influence of readily oxidated metals and hydrated acids, by the supposition that the metal replaces the hydrogen of the combined water. But there exist acids of which we have no known hydrate, equivalent for equivalent, carbonic, chromic, &c. acids. These being destitute of combined water do not admit of similar substitution; no hydrogen being combined, no replacement can take place.

Any theory, to be perfect, must include all known cases; and hence, if this hypothesis is not applicable to all oxygen salts, to the same extent as former views, it fails in its promised advantages. It has not yet been carried out or exhibited in detail by its advocates, which would seem to show they are aware of its difficulties, and are not yet prepared to obviate them. One of the points requiring explanation is the supposition in some of the examples quoted, that potassium and oxygen, two elements occupying the extremes of the electro-chemical series, can be placed in contact with each other without combining, a supposition requiring a subversion of chemical affinity which does not correspond with known facts.

It is not evident why "oxygen-acid salts alone are affected by this discussion." The compounds of sulphur, selenium, &c. are very analogous in character; and as sulphur-acids, combine only with sulphur bases, the same transfer of sulphur will be here required as of oxygen in the former salts, giving rise to as many new sulphur salt-radicals as those of oxygen.—R. B.]

Without deciding definitively in favour of one or other of the rival theories, it is well to keep in view that the great class of salts includes compounds which differ essentially in their capacity of analytical decomposition. A certain number of salts contain salt-radicals which can be isolated, others oxygen-acids which can be isolated, while others have yet afforded neither salt-radical nor acid in a separate state. Hence, they may be classed as—

1. Salts of isolable salt-radicals: chlorides, cyanides, sulphocyanides, &c.
2. Salts of isolable acids: sulphates, nitrates, carbonates, &c.
3. Salts which contain neither an isolable salt-radical nor an isolable acid: acetates, hyposulphites, &c. Even admitting that all salts have the same constitution, the capability of breaking up in such different ways must affect their modes of decomposition in different circumstances, and produce differences in properties which render such distinctions important.

It has become further necessary to recognize three classes of oxygen-acid salts, which in the language of the acid theory contain one, two, and three equivalents of base to one of acid.

1. *Monobasic salts.*—The great proportion of acids, such as sulphuric, nitric, &c. neutralize but one equivalent of base, or more correctly combine in the proportion of one equivalent of acid to each equivalent of oxygen in the base, and form, therefore, *mono*basic salts. (See formulæ of the neutral sulphates, page 158). But this is not inconsistent with an acid forming two series of salts with the same base or class of isomorphous bases. Thus there appear to be two well-marked classes of sulphates of the magnesian oxides, which agree in having one equivalent of base, but differ essentially in the proportions of combined water which they affect. In one series the sulphate is combined with one, three, five, or seven equivalents of water. Copperas (a sulphate of iron), Epsom salt (a sulphate of magnesia), blue vitriol (a sulphate of copper), and most of the well-known magnesian sulphates, belong to this class, which may be called the copperas class of sulphates. All the members of it are very soluble in water, and form double salts with sulphate of potassa. The other series affect two, four, and six equivalents of water. They are less known, but appear to be of sparing solubility, and to be incapable of forming double salts with sulphate of potassa. Gypsum or sulphate of lime belongs to this class, which may, therefore, be called the gypsum class of magnesian sulphates. Sulphate of iron is said to crystallize from solution in sulphuric acid with two equivalents of water, with the crystalline form and sparing solubility of gypsum. Dr. Kane obtained a sulphate of copper with four equivalents of water, by exposing the anhydrous salt to the vapour of hydrochloric acid, which appears to be the second term in this series; and Mitscherlich still maintains the existence of a peculiar sulphate of magnesia containing six equivalents of water of crystallization, which will constitute the third term. It is evident that the cause of such double classes of salts is as deeply seated as that of dimorphism, and hence, possibly, the magnesian sulphate itself, which exists in the two classes, is not the same in its constitution with reference to heat.

2. *Bibasic salts.*—That class of phosphates which received the name of pyrophosphates, was the first in which one equivalent of acid was found to neutralize two equivalents of base; their formulæ being $2RO, PO_5$. The classes of tartrates and racemates which have long been known to chemists, are also bibasic salts. It is the character of a bibasic acid to unite at once with two different bases of the same natural family, which accounts for the formation of Rochelle salt, the tartrate of potassa and soda, of which the formula is $KO, NaO + C_8H_4O_{10}$. It has also been shown that gallic acid is bibasic, the gallate of lead being thus composed: $2PbO + C_7HO_3$. Now if we attempt to make this a monobasic salt by dividing the equivalents both in base and acid by two, an equivalent of gallic acid would come to contain half an equivalent of hydrogen, which Liebig considers as conclusive against the division of its atomic weight. Itaconic, comenic, euchronic, fulminic, and several other organic bibasic acids, might be named. The compound acids formed by the union of two others, and called copulated acids, such as hyposulphobenzoic acid, are usually of this class.

3. *Tribasic salts.*—The tribasic phosphates of the formula $3RO, PO_5$, have likewise proved to be the type of a class of salts. One equivalent of arsenic acid neutralizes three equivalents of base; so, it is probable, does one atom of phosphorous acid. Tannic acid also saturates three atoms of base, the formula of the tannate of lead being $3PbO + C_{18}H_5O_9$ (Liebig). There is the same necessity to admit that citric acid is tribasic, and the formula of a citrate $3RO + C_{12}H_5O_{11}$, as there is to allow that gallic acid is bibasic. Most of the citrates contain two equivalents of fixed base and one of water, but the citrate of silver contains three equivalents of oxide of silver. Cyanuric, meconic, camphoric, and several other organic acids, are tribasic.

Two of the three atoms of base in this class of salts may be different, as is observed in certain citrates, cyanurates, and phosphates, or the whole three may be different, as in the phosphate called microcosmic salt, which contains at once soda, oxide of ammonium, and water as bases.[1] Two or more of the bases may likewise be isomorphous, or at least belong to the same natural family as soda and oxide of ammonium, water, and magnesia.

Salts usually denominated Subsalts.—The preceding classes of salts, and many other bodies also, are capable of combining with a certain proportion of water, generally vaguely spoken of as water of crystallization. The compounds of the present class appear to be salts which have assumed a fixed metallic oxide in the place of this water. They may, therefore, be truly neutral in composition, the excess of oxide not standing in the relation of base to the acid. It appears that the formulæ of the nitrates named are as follows:—

Nitrate of water (acid of sp. gr. 1.42)........HO, NO_5+3HO.
Nitrate of copper (prismatic)...................CuO, NO_5+3HO.
Nitrate of copper (rhomboidal)................CuO, NO_5+6HO.
Subnitrate of copper...............................$CuO, NO_5+3(CuO, HO)$.

I have distinguished as *constitutional* the three atoms of water which exist in these and all the magnesian nitrates, and which are replaced by three atoms of hydrated oxide of copper in the subnitrate of copper, which is therefore a nitrate of copper, with the addition of constitutional (not basic) oxide of copper; a view which is expressed by the arrangement of the symbols in its formula.

The subnitrates of zinc and lead, and probably also those of nickel and cobalt, have a similar composition (Gerhardt). A similar correspondence is observed between the crystallized neutral sulphate of copper, and the subsulphate of copper, containing four equivalents of oxide of copper, and five of water to one of acid:—

Sulphate of copper, $CuO, SO_3, HO+4HO$.
Subsulphate of copper, $CuO, SO_3, (CuO, HO)+2\,(CuO, HO)+2HO$.

Three equivalents of water in the neutral salt appear to be replaced by three equivalents of hydrated oxide of copper in the subsalt. The remaining 2HO of the latter salt are expelled by a moderate heat, while the other 4HO in combination with oxide of copper, are extricated by a much higher temperature, and their separation attended by a palpable decomposition of the salt, as it affords a portion of soluble neutral salt afterwards to water. The remark is made by M. Gerhardt, that the number of such subsalts is greatly exaggerated, which is quite in accordance with my own observations; few salts combining with an excess of oxide in more than one or two proportions. Most subsalts are entirely insoluble in water, but when they possess a certain degree of solubility, they may afford other analogous subsalts by double decomposition. Thus a solution of bisubnitrate of lead, PbO, NO_5+PbO, HO, on the addition of neutral chromate of potassa allows the red bisubchromate of lead, PbO, CrO_3+PbO, to precipitate. M. Gerhardt, who observed this fact, considers that it assimilates the nitrates and pyrophosphates, and indicates that the latter are ordinary subsalts. But this is really a coincidence of small importance, while nitric acid affords no bibasic hydrate, nor a bibasic salt of soda, as phosphoric acid does.

Water, oxide of copper, oxide of lead, and the hydrates of these metallic oxides, appear to be the bodies most disposed to attach themselves to salts in this manner. The strong alkalies, potassa and soda, are never found in such a relation, or discharging any other function than that of base to the acid of the salt. These views of subsalts, in which their constitutional neutrality is preserved, have been extended to organic compounds. Many neutral organic bodies appear to be capable of combining with metallic oxides, particularly with oxide of lead—such as sugar, amidin, dextrin, orcin, and they generally combine with several atoms of the oxide. Thus in the compound of orcin and oxide of lead, $C_{18}H_7O_3+5PbO$, the orcin is combined

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[1] Inquiries respecting the Constitution of Salts; of oxalates, nitrates, phosphates, sulphates, and chlorides. Phil. Trans. 1837, page 47.

with five atoms of constitutional oxide of lead, which actually replace five atoms of constitutional water, which orcin in its ordinary state contains.

Constitutional water is sometimes replaced by a *salt*, which never happens with basic water. Thus cane sugar may be represented as $C_{12}H_{11}O_{11}$, or rather $C_{24}H_{22}O_{22}$; of which one atom of water may be replaced by chloride of sodium, and the compound formed, $C_{24}H_{21}O_{21}+NaCl$. It is to be observed that constitutional water is superadded to a salt, and such an element is removed and replaced without affecting the structure of the body to which it is attached. The replacing substance may also be a compound of a very different character from water; for besides metallic oxides and salts, ammonia and certain anhydrous acids appear to be capable of attaching themselves to salts, in the same manner as constitutional water.

A different view of the constitution of subsalts is advocated by M. Millon, who assumes the existence of poly-atomic bases, or that two, three, four, and even six equivalents of water or a metallic oxide, may together constitute a single equivalent of base, and unite as such with a single equivalent of acid to form a neutral salt (Annales de Chim. et de Phys., xviii. 333).

Salts of the type of red chromate of potassa.—Several salts unite with anhydrous acids. Thus both chloride of sodium and chloride of potassium absorb and combine with two atoms of anhydrous sulphuric acid without decomposition, when exposed to the vapour of that substance. Sulphate of potassa also combines with one atom of anhydrous sulphuric acid. All these compounds are destroyed by water. But the red chromate of potassa, generally called bichromate of potassa, which consists of chromate of potassa together with one atom of chromic acid, is possessed of greater stability, as is likewise the compound of chloride of sodium or potassium with two atoms of chromic acid. Another compound containing one atom of potassium and three atoms of chromic acid, known as the terchromate of potassa, may be viewed as a combination of chromate of potassa with two atoms of chromic acid, and represented by KO, CrO_3+2CrO_3. The bichromate of potassa will then be KO, CrO_3+CrO_3, and the chromate containing chloride of potassium, $KCl+2CrO_3$. The biniodate of potassa (iodate of water and potassa) may be rendered anhydrous, and, when so, is a salt of the same class.

Double salts.—Salts combine with each other, but by no means indiscriminately. With a few exceptions, which may be placed out of consideration for the present, the combining salts have always the same acid—sulphates combining with sulphates, chlorides with chlorides. Their bases or their metals, however, must belong to different natural families. Thus it may be questioned whether a salt of potassa ever combines with a salt of soda, certainly never with a salt of ammonia. Salts of the numerous metals including hydrogen, belonging to the magnesian family, do not combine together. Thus sulphate of magnesia does not form a double salt with sulphate of lime, with sulphate of zinc, or with sulphate of water; while on the other hand salts of this family are much disposed to combine with salts of the potassium family — sulphate of soda, for instance, forming double salts with sulphate of lime, sulphate of zinc, and sulphate of water. We have thus the means of distinguishing between a double salt, and the salt of a bibasic or tribasic acid. The bisulphate and binoxalate of potassa saturated with soda, form sulphates and oxalates of potassa and soda, which separate from each other by crystallization, although the acid salts are themselves double salts of water and potassa. But the acid fulminate of silver, or the acid tartrate of potassa (bitartrate), affords only one salt when saturated with soda, in which isomorphous bases exist, and which, therefore, is a salt of one acid, and not a compound of two salts. The great proportion of the salts which are named *super*, *acid* and *bi*-salts, contain a salt of water, and are double salts — such as the supercarbonate of soda (HO, CO_2+NaO,CO_2), the bisulphate of potassa (HO, SO_3+KO, SO_3), and the binacetate of soda: but a few of them are bibasic or tribasic salts, containing one or two atoms of water as base — such as the salt called bitartrate of potassa, or biphosphate of potassa ($2HO, KO+PO_5$).

From these observations must be excepted double salts formed by fusion, and many salts formed in highly acid solutions, which are scarcely limited in variety of composition; carbonate of potassa fusing with the carbonate or sulphate of soda, and sulphate of baryta crystallizing in combination with sulphate of water, from solution in sulphuric acid. Such salts are decomposed by water, and are otherwise deficient in stability, compared with the soluble double salts, to which alone the preceding remarks apply.

There is no parallelism between the constitution of a double salt and that of a simple salt itself, or foundation for the statements which are sometimes made, that one of the salts which compose a double salt has the relation to the other of an acid to a base, and that one salt is electro-negative to the other. The resolution of a double salt into its constituent salts by electricity, has never been exhibited, and is not to be expected, from what is known of electrolytic action; while no analogy whatever subsists between a double salt and a simple salt on the binary view of the constitution of the latter. Besides, the supposed analogy is destroyed by what is known of the derivation of double salts. Sulphate of magnesia acquires an atom of sulphate of potassa in the place of an atom of water, which is strongly attached to it, in becoming the double sulphate of magnesia and potassa. In the same way, the sulphate of water has an atom of water also replaced by sulphate of potassa, in becoming the bisulphate of potassa; relations which appear in the rational formulæ of these salts:

Sulphate of magnesia....................................	$\dot{M}g\dddot{S}(\dot{H})+6\dot{H}$
Sulphate of magnesia and potassa....................	$\dot{M}g\dddot{S}(\dot{K}\dddot{S})+6\dot{H}$
Sulphate of water (acid of sp. gr. 1.78)............	$\dot{H}\dddot{S}(\dot{H})$
Bisulphate of potassa....................................	$\dot{H}\dddot{S}(\dot{K}\dddot{S})$

It thus appears that a provision exists in sulphate of magnesia itself for the formation of a double salt, and that the molecular structure is unaltered, notwithstanding the assumption of the sulphate of potassa as a constituent. The derivation of the acid oxalates likewise throws much light on the nature of double salts. The oxalate of potassa contains an atom of constitutional water, which is replaced by hydrated oxalic acid (the crystallized oxalate of water), in the formation of the binoxalate of potassa (double oxalate of potassa and water), or by the oxalate of copper in the formation of the double oxalate of potassa and copper, as exhibited in the following formulæ, in which the replacing substances are enclosed in brackets to mark them as before:

Oxalate of potassa..	$\dot{K}\dddot{C}C, (\dot{H})$
Binoxalate of potassa.....................................	$\dot{K}\dddot{C}C, (\dot{H}\dddot{C}CH_2)$
Oxalate of potassa and copper	$\dot{K}\dddot{C}C, (\dot{C}u\dddot{C}C\dot{H}_2)$

Now the anomalous salt, quadroxalate of potassa, is derived in the same way from the binoxalate, as the binoxalate itself is derived from the neutral oxalate, two atoms of water being displaced by two atoms of hydrated oxalic acid, thus:

Binoxalate of potassa...................................	$\dot{K}\dddot{C}C, \dot{H}\dddot{C}C, (2H)$
Quadroxalate of potassa................................	$\dot{K}\dddot{C}C, \dot{H}\dddot{C}C, (2\dot{H}\dddot{C}CH_2)$

These examples illustrate the derivation of double salts by *substitution.* The structure of the salts, too, exemplifies what may be called *consecutive* combination. The basis of the last mentioned salt, for instance, is oxalate of potassa, which is in direct combination with oxalate of water. A compound body is thus produced which seems to unite *as a whole* with two atoms of hydrated oxalic acid. This is very different from the direct combination of all the elements which compose the salt.

In the formation of many other classes of double salts, no substitution is observed, but simply the attachment of two salts together, often of an anhydrous with a hydrated salt, in which case the last often carries its combined water along with it, and sometimes acquires an additional proportion. Thus in the formula of the double chloride of potassium and copper, $KCl + CuCl, 2HO$, the formulæ of its constituent salts reappear without alteration; and in that of alum, sulphate of potassa is found with the hydrated sulphate of alumina annexed, of which the water is increased from eighteen to twenty-four atoms. In these and all other double salts, the characters of the constituent salts are very little affected by their state of union. If one of them has an acid reaction, like sulphate of alumina or chloride of copper, it retains the same character in combination; and nothing resembling a mutual neutralization of the salts by each other is ever observed. No heat is evolved in their formation. (Memoirs of the Chemical Society, ii. 51).

The compounds of chlorides with chlorides, and of iodides with iodides, are numerous, and were viewed by Bonsdorf as simple salts, in which one of the chlorides is the acid, and the other the base. But such an opinion can no longer be entertained, the chlorides themselves being unquestionably salts, and their compounds, therefore, double salts.

The combinations of such salts with each other as contain different acids are not so well understood, the theory of their formation having hitherto been little attended to. They are in general decomposed by water, and easily, if the solubility of one of their constituents is considerable, as is observed of the compounds of iodate of soda with one and with two proportions of chloride of sodium, of the biniodate of potassa with the sulphate of potassa, of the oxalate of lime with the chloride of calcium.

The compound cyanides, which form a considerable class of salts, must be excepted from all the preceding general statements in regard to double salts. Cyanides of the same family combine together, as cyanide of iron with cyanide of hydrogen; the compound cyanide also generally consists of three and not of two simple cyanides; and lastly, the properties of compound cyanides are very different from those of the simple cyanides which are supposed to compose them. The simple cyanide of potassium, for instance, is highly poisonous, while the double cyanide of potassium and iron is as mild in its action upon the animal economy as sulphate of soda. But the compound cyanides may be removed from the class of double salts, on a speculative view of their constitution which their anomalous character led me to propose. It is to be premised that the supposed double proto-cyanide of iron and potassium (yellow prussiate of potassa) affords no hydrocyanic acid whatever when distilled with an excess of sulphuric acid at a temperature not exceeding 100°; which suggests the idea that it does not contain cyanides or cyanogen. Assuming the existence of a new compound radical, N_3C_6, which has three times the atomic weight of cyanogen, and may be called *prussine*, and which is also *tribasylous* or capable of combining with three atoms of hydrogen or metal, like the radical of the tribasic class of phosphates, then the compound cyanides assume a constitution of extreme simplicity. We have one atom of prussine combined always with three atoms of hydrogen or metal in the following salts: in the proto-cyanide of iron and potassium with one of iron and two of potassium; in the componnd called ferro-cyanic acid, with one of iron and two of hydrogen; in Mosander's salts, with one of iron, one of potassium and one of barium, calcium, &c.; with two of iron and one of potassium in the salt which precipitates on distilling the yellow prussiate of potassa with sulphuric acid at 212°. To many of these, parallel combinations might be adduced from the tribasic phosphates. Prussides likewise combine together, producing double prussides, such as

Percyanide of iron and potassium (red prussiate of potassa)…….	$Fe_2, N_3C_6 + K_3, N_3C_6$
Prussian blue……………………	$Fe_2, N_3C_6 + Fe_3, N_3C_6$
Basic prussian blue…………….	$Fe_2, N_3C_6 + Fe_3, N_3C_6 + Fe_2O_3$

Formation of salts by substitution. — Chemists have come to pronounce less decidedly on theories of the constitution of salts and the arrangement of elements in these and other compounds, since their attention has been fixed upon the formation of compounds, by the subtitution of one element for another, without injury to the original form or type, and often to give a preference to empirical over rational formulæ, while their opinions on chemical constitution were suspended. The elementary composition of oil of vitriol, or the hydric sulphate, is expressed by SO_4H; the sulphate type, and other neutral sulphates, are formed by replacing the hydrogen by a metal; the zinc sulphate, SO_4Zn; the soda sulphate, SO_4Na. M. Gerhardt, assuming as a law that the equivalent of all compound bodies gives two volumes of vapour, divides the equivalents of the following elements by two — nitrogen, phosphorus, chlorine, hydrogen, and all the metals; and is thereby enabled to construct substitution formulæ, which are often remarkable for their simplicity. This will appear in the following selected formulæ: —

FORMULÆ BY M. GERHARDT.

($O=8$, $S=16$; *the other symbols = half the usual equivalents.*)

I. NITRATES.

Hydric nitrate	NO_3H	Monobasylous salts.
Magnesia nitrate	NO_3Mg	
Potassa nitrate	NO_3K	

II. SULPHATES.

Hydric sulphate	SO_4H_2	Bibasylous salts.
Magnesia sulphate	SO_4Mg_2	
Potassa sulphate	SO_4K_2	
Potassa bisulphate	SO_4KH	

III. TRIBASIC PHOSPHATES.

Hydric phosphate	PO_4H_3	Tribasylous salts.
Subphosphate of soda	PO_4Na_3	
Phosphate of soda	PO_4Na_2H	
Biphosphate of soda	PO_4NaH_2	

The preceding groups are symbolized without any division of the equivalents used; but M. Gerhardt departs from this practice, when necessary, in the *unitary* system of notation which he recommends: —

Anhydrous alum	$SO_4\ (K_{\frac{1}{2}}Al_{\frac{3}{2}})$
Pyrophosphate of soda	$PO_{\frac{7}{2}}\ (Na_2)$
Subphosphate of soda + HO	$PO_{\frac{9}{2}}\ (Na_3H)$

Although a rational formula, strictly speaking, expresses no more than a decomposition, — and the rational formulæ of a compound may truly, therefore, be as numerous as the modes of decomposition of which it is susceptible, — still much would undoubtedly be lost by abandoning such formulæ for formulæ which are entirely empirical; unless, indeed, it is found that the uniform practice of exhibiting the leading constituent, in the proportion of a single equivalent, should bring together different bodies under common formulæ, which are types of useful classification, as M. Gerhardt maintains.

Salts of Ammonia. — Ammonia is a gaseous compound of one equivalent of nitrogen and three of hydrogen, of which the solution in water is caustic and alkaline, and which neutralizes acids perfectly, as potassa and soda do. But all its oxygen-acid salts contain, besides ammonia, an equivalent of water which is essential to them, and inseparable without the destruction of the salt; and with this additional constituent they are isomorphous with the salts of potassa. Hydrochloric acid also unites with ammonia without losing its hydrogen, and the compound or hydrochlorate of ammonia, which is isomorphous with the chloride of potassium, contains, therefore, an equivalent of hydrogen, besides chlorine and ammonia. On the now generally received theory of these salts, the ammonia with this hydrogen, or that of the water in the oxygen-acid salts, constitutes a hypothetical basyl, *ammonium* (NH_4), to which allusion has already been made as being isomorphous with potassium. This view of the constitution of the salts of ammonia will be made obvious by a few examples:—

	ON THE AMMONIUM THEORY.
Hydrochlorate of ammonia, HN_3, HCl	Chloride of ammonium, NH_4, Cl
Sulphate of ammonia, NH_3, HO, SO_3	Sulphate of oxide of ammonium, NH_4O, SO_3
Nitrate of ammonia, NH_3 HO, NO_5	Nitrate of oxide of ammonium, NH_4O, NO_5

The application of this theory to the compounds of ammonia with hydrosulphuric acid and sulphur is particularly felicitous. These compounds may be thus represented, and placed in comparison with their potassium analogues, NH_4 being equivalent to K:—

Sulphide of ammonium	NH_4S	KS
Sulphide of ammonium and hydrogen (bihydrosulphate of ammonia	NH_4S, HS	KS, HS
Tritosulphide of ammonium	NH_4S_3	KS_3
Pentasulphide of ammonium	NH_4S_5	KS_5

Ammonium is supposed to present itself in a tangible form, and in possession of metallic characters, in the formation of what is called the *ammoniacal amalgam.* When mercury alloyed with one per cent. of sodium is poured into a saturated cold solution of sal ammoniac (chloride of ammonium), it undergoes a prodigious increase of bulk, expanding sometimes from one volume to two hundred volumes, without becoming in the least degree vesicular, and acquiring a butyraceous consistence, while its metallic lustre is not impaired. A small addition is at the same time made to its weight, estimated at from 1 part in 2000 to 1 in 10,000, which certainly consists of ammonia and hydrogen in the proportions of ammonium. The sodium, it is supposed, combines with the chlorine of chloride of ammonium, and the liberated ammonium with mercury, so that the metallic product is an amalgam of ammonium. It speedily resolves itself again spontaneously into running mercury, ammonia, and hydrogen, unless the temperature be reduced so far as to freeze it. After all, however, neither isolation nor the metallic character is essential to ammonium as an alkaline radical, other basyls being now admitted, such as ethyl and benzoyl, which have no claim to such characters.

Other classes of ammoniacal salts may be formed in which the fourth equivalent of hydrogen in ammonium is replaced by a metal of the magnesian family,—by copper in particular, which most resembles hydrogen. Thus anhydrous chloride of copper absorbs a single equivalent of ammonia with great avidity and the evolution of much heat, which cannot afterwards be separated from it by the agency of heat. The compound appears to be strictly analogous to chloride of ammonium, but contains an equivalent of copper in the place of hydrogen. Its formula is NH_3Cu, Cl, and it may be named the chloride of *cuprammonium.* This salt and many others are likewise capable of combining with more ammonia, which is retained less strongly, and has the relation of constitutional water to the salt. The constitution of these combinations will be more minutely considered in other parts of the work.

Amidogen and amides.—The existence of another compound of nitrogen and hydrogen (NH_2), containing an equivalent less of hydrogen than ammonia, is recognized in an important series of saline compounds, although it has not been isolated. These compounds are called *amides,* and hence the name amidogen applied to their radical. When potassium is heated in ammoniacal gas, the metal is converted into a fusible green matter, which is the amide of potassium, while an equivalent of hydrogen is disengaged. Amidogen exists also in the white precipitate of mercury formed on adding ammonia to corrosive sublimate, the product being a double chloride and amide of mercury ($HgCl + HgNH_2$).

Amides are produced in an interesting way, by the abstraction of the elements of water from compounds of ammonia with oxygen acids. Thus, on decomposing oxalate of ammonia by heat, the acid losing a proportion of oxygen, and the ammonia a proportion of hydrogen, *oxamide* sublimes, which consists of $NH_2 + 2CO$. When ammoniacal gas and anhydrous sulphuric acid vapour are mixed together, a saline substance is produced which dissolves in water, but is not sulphate of ammonia, the solution affording no indications of sulphuric acid. It is believed to be a hydrated *sulphamide*, or to be constituted thus, $NH_2, SO_2 + HO$; a compound which it will be observed contains neither ammonia nor sulphuric acid. Similar products result from the action of ammonia on dry carbonic acid and all the other anhydrous oxygen salts. The difference between these compounds and the true salts of ammonia affords an argument in favour of the ammonium theory of the latter.

ANTITHETIC OR POLAR FORMULÆ.

Formulæ for compounds may be constructed to exhibit the attraction of the ultimate elements for each other without involving any contested theory of the constitution of compounds, and which indeed might supersede the consideration of such views, were it not that the nomenclature, which it would be inconvenient to alter greatly, is founded upon the latter. A certain amount of information is given in the ordinary formulæ by the arrangement of the symbols, the symbol of the basylous or positive constituent being placed before the symbol of the halogenous or negative constituent, as in HO for water, SO_3 for sulphuric acid. To carry out this principle farther, and make its application more perspicuous, I have suggested the writing of a formula in two lines, placing all the negative constituents in the upper, and the positive in the lower line:—

Potassa....... $\frac{O}{K}$ Water....... $\frac{O}{H}$ Sulphuric acid.... $\frac{O_3}{S}$ Ammonia........ $\frac{N}{H_3}$

Cyanogen.... $\frac{N}{C_2}$ Olefiant gas $\frac{H_4}{C_4}$ Carbonic oxide... $\frac{O_2}{C_2}$ Hydric oxalate $\frac{O_3O}{C_2H}$

From their construction these formulæ are named *antithetic*, the two orders of constituents being placed opposite or against each other; or *polar*, from exhibiting the opposite attractive forces of the elements. Several decompositions already referred to, and others, may be made more intelligible by their aid.

Decomposition of ammoniacal salts.—In the decomposition of oxalate of ammonia and formation of oxamide, the change consists in the abstraction of two equivalents of water from the constituents of the salt: the formulæ being—

Oxalate of ammonia.................... $\frac{NOO_3}{H_3HC_2} - \frac{O_2}{H_2} = \frac{NO_2}{H_2C_2}$ oxamide.

The interesting observation has lately been made by M. Dumas, that by distillation with anhydrous phosphoric acid, four equivalents of water are separated from oxalate of ammonia, and cyanogen formed. Supposing that the formation of oxamide precedes this last decomposition, we have—

Oxamide................................ $\frac{NO_2}{H_2C_2} - \frac{O_2}{H_2} = \frac{N}{C_2}$ cyanogen.

It is seen, that although we cannot say that water exists either in oxalate of ammonia or in oxamide, still 4O is negative and 4H positive in the first of these substances, and 2O negative with 2H positive in the second, the relation which these elements bear to each other in water. The polar relation of these elements, therefore, does not require to be subverted, when they are led to unite and take the form of water, under the influence of the attraction of phosphoric acid for that oxide. It is manifestly a law of decomposition that those decompositions take place most readily which permit the elements to continue in their original polar condition and position in the formulæ; the explanation being, that such decompositions are promoted by the peculiar attractions of the ultimate elements for each other as they exist in the original compound; or the compound molecule is broken up in the direction in which it naturally divides.

The decomposition by phosphoric acid of other salts of ammonia containing acids related to the alcohols, illustrates the same constancy of polar relation in the elements before and after the change. Thus, formiate of ammonia gives hydrocyanic acid by the abstraction of four equivalents of water: —

$$\text{Formiate of ammonia......} \ \frac{N\ O}{H_3H}\frac{HO_3}{C_2} - \frac{O_4}{H_4} = \frac{NH}{C_2} \ \text{hydrocyanic acid.}$$

Here the hydrogen of hydrocyanic acid is represented as negative, and it can certainly be replaced by chlorine, a negative element, and the chloride of cyanogen formed: —

$$\text{Hydrocyanic acid............} \ \frac{NH}{C_2} \quad \text{Chloride of cyanogen.........} \ \frac{NCl}{C_2}$$

With a metallic oxide, however, hydrocyanic acid gives a cyanide, and then the hydrogen appears positive —

$$\text{Hydrocyanic acid............} \ \frac{N}{C_2H} \quad \text{Cyanide of silver............} \ \frac{N}{C_2Ag}$$

But hydrocyanic acid is in the lowest degree feeble in its powers as an acid, or as cyanide of hydrogen, and its hydrogen appears to be just on the limit between the basylous and halogenous character and position.

Acetate of ammonia distilled with phosphoric acid also loses four equivalents of water, like all the ammoniacal salts in question, and gives the cyanide of methyl:—

$$\text{Acetate of ammonia} \ \frac{N\ O}{H_3H}\frac{O_3H_3}{C_4} - \frac{O_4}{H_4} = \frac{H_2H}{C_2}\frac{N}{C_2} \ \text{cyanide of methyl.}$$

The chloracetate of ammonia in losing 4HO gives a liquid body of the composition C_4Cl_3N: —

$$\text{Chloracetate of ammonia...............} \ \frac{N\ O}{H_3H}\frac{O_3Cl_3}{C_4} - \frac{O_4}{H_4} = \frac{Cl_2}{C_2}\frac{ClN}{C_2}$$

Here the single negative H of hydrocyanic acid is also under the positive attraction of the C_2 of the hydrocarbon, C_2H_2, a cross attraction, which forms a bond of union between the hydrocyanic acid and hydrocarbon, and supports the equilibrium.

Why is ammonia a base?—Of ammonia and hydrochloric acid the antithetic formulæ are—

$$\frac{N}{H_3} \ \text{and} \ \frac{Cl}{H}$$

There can be little doubt but that when these bodies are united, the highly negative chlorine shares, or assumes entirely, the positive attraction of the third equivalent of hydrogen in ammonia, which there is reason to believe is less powerfully attracted or neutralized by the negative nitrogen than the other two equivalents of hydrogen. We thus obtain the following formula:—

$$\text{Hydrochlorate of ammonia........................} \ \frac{N\ \ Cl}{H_2\ H_2}$$

Now the acid character of hydrochloric acid, which is neutralized in the salt, depends upon the former substance being a compound in which a powerful salt-radical, chlorine, is united with a weak basyl, hydrogen. With a powerful basyl, such as potassium, chlorine gives a neutral salt, the chloride of potassium. But it is probable that the subchloride of hydrogen, H_2Cl, if it could exist in a separate state, would be an equally neutral salt, for hydrogen belongs to the magnesian class of elements, two atoms of which appear to be equivalent to one atom of the potassium class, or H_2Cl to be equivalent to KCl, and possibly isomorphous with it. One atom of nitrogen there are also grounds for believing to be equivalent in composition to two atoms of oxygen, or $N=2O$. Hence the compound $\frac{N}{H_2}$ has a character of saturation, or polar neutralization, like $\frac{O_2}{H_2}$ or two equivalents of water. In ammonia, therefore, the third basylous atom of hydrogen may well be considered as unsaturated, and to be what imparts a basylous or positive character and activity to the compound. In metallic oxides which are bases, we have also the positive property of the metal imperfectly saturated by the weak negative body oxygen, and the positive attraction therefore in excess.

In the oxygen acids, on the contrary, there is an excess of negative attraction from the predominance of the oxygen element, and it is remarkable that in the more powerful acids, such as sulphuric, nitric, and chloric, one equivalent of this oxygen is but feebly united, and its negative attraction free to act, like the positive attraction of the third equivalent of hydrogen in ammonia. Hence ammonia and anhydrous sulphuric acid readily combine:—

$$\frac{N}{H_2H} + \frac{OO_2}{S} = \frac{N}{H_2}\frac{O}{H}\frac{O_2}{S}$$

From the action of the affinities exhibited in the last formula, a stable equilibrium results; but it is not intended to express that amidogen, water, and sulphurous acid, exist ready formed in the compound. Indeed, in no case do the formulæ express actual formation of subordinate compounds, or anything more than what are considered to be the predominating set of attractions among all the possible attractions which the elements have for each other, and all of which they continue to exert in some degree.

In sulphate of oxide of ammonium, the affinities of equilibrium are those of the elements of amidogen, suboxide of hydrogen, and sulphuric acid:—

Constitution of Sulphate of Ammonia. Sulphate of Ammonia.

$$\frac{N}{H_2} + \frac{O}{H} + \frac{O_3}{S} = \frac{N}{H_2}\frac{O}{H_2}\frac{O_3}{S}$$

In this and all the other oxygen-acid salts of ammonia, the highly alkaline oxide H_2O appears, and constitutes the point of attachment for the acid. Other sources of stability in the sulphate of ammonia are — first, the attraction of N for its third atom of hydrogen, which is never entirely relinquished, although the latter is more under the influence of the O of the water; and, secondly, the attraction of the O_3 of the sulphuric acid for the basylous H_2: for these cross attractions prevent the division of the compound into subordinate compounds under the influence of the predominating affinities first enumerated. This salt may be taken as a fair example of the assumed mode of formation of compounds, in which the affinities of the elementary atoms only are operative, to the entire exclusion of the affinities usually assigned to subordinate groups of elements acting as compound radicals or quasi-elements.

Why are arsenic and phosphoric acids tribasic?—Phosphoric acid, PO_5, may be considered, from its properties and mode of formation, as phosphorous acid, PO_3 + two equivalents of oxygen less strongly combined; and in the same way arsenic acid, AsO_5, as arsenious acid, AsO_3 + two equivalents of oxygen. Now, when united with a base, which we shall suppose a metallic protoxide, RO, these two surplus equivalents of oxygen in the phosphoric acid, added to the single equivalent of oxygen in the base, convert an equivalent of the latter into an acid of the formula RO_3. Two more equivalents of base are required—one to neutralize this RO_3, and the other to neutralize the phosphorous acid, PO_3; making three equivalents of base to every single equivalent of phosphoric acid. The general formula for a so-called tribasic phosphate is, therefore—

Phosphate............................... $\frac{O\ O_3}{R\ R} + \frac{O\ O_3}{R\ P}$

and resembles a double sulphate, $RO, SO_3 + RO, SO_3$.

Tribasic subphosphate of lime ($3CaO, PO_5$)............... $\frac{O\ O_3}{Ca\ Ca}\frac{O\ O_3}{Ca\ P}$

Phosphoric acid appears farther to have the power, when heated strongly, of assuming the two equivalents of oxygen referred to into a more intimate state of combination, possibly with the loss of a portion of combined heat, and gives the class of monobasic metaphosphates. The general formula of a metaphosphate is—

Metaphosphate....................................... $\frac{O\ O_5}{R\ P}$

A pyrophosphate, or so-called bibasic phosphate, is, on this view, a compound of a common phosphate and metaphosphate :—

Pyrophosphate.................................... $\frac{O\ O_3}{R\ R}\frac{O\ O_3}{R\ P} + \frac{O\ O_3}{R\ P}$

Hence the equivalent of a pyrophospate contains four equivalents of base and two of phosphoric acid—the reason why so many double pyrophosphates appear to exist.

Phosphoric acid is thus supposed to resemble those conjugate organic acids which combine with two equivalents of base, because they possess the elements of two different acids.

ATOMIC VOLUME OF SOLID BODIES.

Since the existence of simple relations between the combining volumes of gaseous bodies was ascertained by Gay-Lussac, various attempts have been made to establish similar relations between the measures, as well as the weights, in which bodies, in the liquid and solid form, enter into combination. If the atoms of all elements had, in the solid form, the same bulk, their specific gravities would be regulated by their atomic weights, and be in the same proportion. It was early observed by M. Dumas, that a close approximation to this simple ratio holds among the specific gravities of a considerable number of isomorphous bodies; but it is by no means general. The subject has received its fullest investigation from Professor Schroeder of Mannheim[1], Dr. Hermann Kopp[2] of Giessen, and Messrs. Playfair and Joule.[3] Much information has been collected, and many curious relations in the specific gravities of particular bodies pointed out; but the general deductions drawn can, in general, claim only a certain degree of probability. Much of the uncertainty arises from the specific gravity of a body in the solid form being often variable between rather wide

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[1] Die Molecularvolume der chemischen Verbindungen im festen und flussigen Zustande Mannheim, 1843.

[2] Bemerkungen zur Volumtheorie, Braunschweig, 1844; Annales de Chimie et de Physique, 2e Sér. T. lxxv. and 3e Sér. T. iv. p. 462.

[3] Memoirs of the Chemical Society of London, vol. ii. p. 401; vol. iii. pp. 57 and 199. Also, a paper on the Constitution of Aqueous Solutions of Acids and Alkalies, by Mr. J. J Griffin; ibid. p. 155.

limits. Thus platinum, in a pulverulent state, reduced from its oxide and from the double chloride of platinum and ammonium respectively, is found to have the specific gravity 17·766 in the first case, and 21·206 in the second (Playfair and Joule); and the effect of compression upon the malleable metals is generally very sensible. As the rate of dilatation of different solids and liquids by heat is very dissimilar, it is obvious their relations in density may also be disturbed or disguised by temperature.

At present, I shall confine myself to a summary of the results of M. Kopp on this subject, which partake least of a speculative character. The *atomic volume*, which I substitute for the *specific volume* of Dr. Kopp, in the following tables, is the volume or measure of an equivalent or atomic proportion of the different substances enumerated. The *calculated density* is obtained by dividing the atomic weight by this volume. Thus an equivalent of mercury, 1266 parts by weight, has the volume 93 assigned to it. Now 1266, divided by 93, gives 13·6 as the "calculated" specific gravity, which coincides with the specific gravity of mercury actually observed by Kupffer and others. The atomic volume for oxygen will afterwards appear to be 16, or a multiple of that number, and is the modulus of the scale.

Table I.

Atomic Volume and Specific Gravity of Elements.

Substances.		Atomic Weight.	Primitive Atomic Volume.	Calculated Sp. Grav.	Observed Specific Gravity.
Antimony......	Sb	806	120	6·72	6·70 Karsten; 6·6 Breithaupt; 6·85 Muschenbroeck.
Arsenic	As	470	80	5·87	5·70, 5·96 Guibourt; 5·62 Karsten; 5·67 Herapath.
Bismuth	Bi	1330	135	9·85	9·88 Thenard; 9·83 Herapath; 9·65 Karsten.
Bromine	Br	489	160	3·06	2·99 Loewig; 2·97 Balard.
Cadmium	Cd	697	81	8·60	8·66 Herapath; 8·63 Karsten, Kopp; 8·60 Stromeyer.
Chlorine	Cl	221	160	1·38	1·33 Faraday.
Chromium	Cr	352	69	5·10	5·10 Thomson.
Cobalt..........	Co	369	44	8·39	8·49 Brunner; 8·51 Berz.; 8·71 Lampadius.
Copper	Cu	396	44	9·00	8·96 Berzelius; 9·00 Muschenb.; 8·72 Karsten.
Cyanogen	Cy	165	160	1·03	About 0·9 Faraday.
Gold	Au	1243	65	19·1	19·26 Brisson.
Iridium.........	Ir	1233	57	21·6	19·5 Mohs; 23·5 Breithaupt; 21·8 Hare.
Iodine	I	789	160	4·93	4·95 Gay-Lussac.
Iron	Fe	339	44	7·70	7·6, 7·8 Broling; 7·79 Karsten.
Lead	Pb	1294	114	11·35	11·33 Kupffer; 11·39 Karsten; 11·35 Herapath.
Manganese....	Mn	346	44	7·86	8·03 Bachmann; 8·01 John.
Mercury	Hg	1266	93	13·6	13·6 Kupffer, Karsten, Cavallo.
Molybdenum .	Mo	599	69	8·68	8·62, 8·64 Bucholz.
Nickel	Ni	370	44	8·41	8·40 Tourte; 8·38 Tupputi; 8·60 Brunner.
Osmium........	Os	1244	57	21·8	Native; 19·5 (?) Thenard.
Palladium	Pd	666	57	11·7	11·3 Wollaston; 12·1 Lowry.
Phosphorus ...	P	196	111	1·77	1·77 Berzelius.
Platinum	Pt	1233	57	21·6	21·0 Borda; 21·5 Berzelius; 23·5 (?) Cloud.
Potassium.....	K	490	583	0·84	0·86 Gay-Lussac, Thenard; 0·87 Sementini.
Rhodium	R	651	57	11·4	11·0 Wollaston; 11·2 Cloud.
Selenium	Se	495	115	4·30	4·30, 4·32 Berzelius; 4·31 Boullay.
Silver..........	Ag	1352	130	10·4	10·4 Karsten.
Sodium.........	Na	291	292	0·99	0·97 Gay-Lussac and Thenard.
Sulphur........	S	201	101	1·99	1·99, 2·05 Karsten; 1·99 Breithaupt.
Tin..............	St	735	101	7·28	7·28 Herapath; 7·29 Kupffer, Karsten.
Titanium	T	304	57	5·33	5·3 Wollaston; 5·28 Karsten.
Tungsten	W	1183	69	17·1	17·2 Allan and Aiken; 17·4 Bucholz.
Zinc	Zn	403	58	6·95	6·92 Karsten; 6·86, 7·21 Berzelius.

It will be observed that certain analogous substances possess the same atomic volume:—bromine, chlorine, cyanogen, and iodine; chromium, molybdenum, and tungsten; cobalt, copper, iron, manganese, and nickel; iridium, osmium, palladium, platinum, and rhodium.

There are also analogous substances of which the atomic volume of one is double that of the other. The volume of an equivalent of silver is double that of gold, and the volume of potassium double that of sodium.

When a substance enters into combination, it either occupies its own volume, or assumes a new volume, which last may remain constant through a class of compounds. Hence the volumes in the preceding table are described as the primitive atomic volumes. The metals enumerated possess the following atomic volumes in their salts:—

	Atomic volume in Salts.
Ammonium	218
Barium	143
Calcium	60
Magnesium	40
Potassium	234
Sodium	130
Strontium	108

The other metals are supposed to retain their primitive volumes in combination.

In explaining the atomic volume of carbonates, it is supposed by Dr. Kopp that the salt-radical CO_3 enters into its combinations with the atomic volume 151.

In the nitrates, the salt-radical NO_6 is supposed to have the atomic volume 358.

In one class of sulphates, SO_4 is supposed to have the atomic volume 236; in another, the atomic volume 186.

In the chromates, the atomic volume of CrO_4 is 228; and, in the tungstates, that of WO_4 is 244.

The atomic volume of chlorine is 196 in one class of chlorides, and 245 in another.

On combining the atomic volumes of the metals contained in the salts with these suppositions for their salt-radicals, the atomic volume of the compound is obtained, and the following calculated specific gravities:—

TABLE II.—*Atomic Volume and Specific Gravity of Salts.*

CARBONATES.

CARBONATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Cadmium	1073	$Cd+CO_3$	81+151=232	4·63	4·42 Herapath; 4·49 K.
Iron	715	$Fe+CO_3$	144+151=195	3·67	3·33 Mohs; 3·87 Naum.
Lead	1670	$Pb+CO_3$	114+151=265	6·30	6·43 Karsten; 6·47 Breithaupt.
Manganese	722	$Mn+CO_3$	44+151=195	3·70	3·55, 3·59 Mohs.
Silver	1728	$Ag+CO_3$	130+151=281	6·15	6·08 Karsten.
Zinc	779	$Zn+CO_3$	58+151=209	3·73	4·44 Mohs; 4·4, 4·5 Naumann.
Baryta	1233	$Ba+CO_3$	143+151=294	4·19	4·30 Karsten; 4·24 Breit.; 4·30 Mohs.
Lime	632	$Ca+CO_3$	60+151=211	3·00	Arragonite 3·00 Breit; 2·93 Mohs. Calc. spar 2·70 Kar.; 2·72 Beudant.
Magnesia	534	$Mg+CO_3$	40+151=191	2·80	2·31 Breithaupt; 3·00, 3·11 Mohs; 2·88, 2·97 Naum.
Potassa	866	$K+CO_3$	234+151=385	2·25	2·26 Karsten.
Soda	667	$Na+CO_3$	130+151=281	2·37	2·47 Karsten.
Strontia	923	$Sr+CO_3$	108+151=259	3·56	3·60 Mohs; 3·62 K.
Dolomite	1166	$Mg+CO_3$ $Ca+CO_3$	40+151 60+151 =402	2·90	2·88 Mohs.
Mesiline	1250	$Mg+CO_3$ $Fe+CO_3$	40+151 44+151 =386	3·24	3·35 Mohs.

NITRATES.

NITRATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Lead	2071	$Pb+NO_6$	114+358=472	4·40	4·40 Karsten; 4·77 Breithaupt; 4·34 Kopp.
Silver	2129	$Ag+NO_6$	130+358=488	4·36	4·36 Karsten.
Ammonia.......	1004	$Am+NO_6$	218+358=576	1·74	1·74 Kopp.
Baryta	1634	$Ba+NO_6$	143+358=501	3·20	3·19 Karsten.
Potassa	1267	$K+NO_6$	234+358=592	2·14	2·10 Karst.; 2·06 Kopp.
Soda	1068	$Na+NO_6$	130+358=488	2·19	2·19 Marx.; 2·20 Kopp. 2·26 Karsten.
Strontia	1324	$Sr+NO_6$	108+358=466	2·84	2·89 Karsten.

SULPHATES: FIRST CLASS.

SULPHATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Copper	997	$Cu+SO_4$	44+236=280	3·56	3·53 Karsten.
Silver	1953	$Ag+SO_4$	130+236=366	5·34	5·34 Karsten.
Zinc	1004	$Zn+SO_4$	58+236=294	3·42	3·40 Karsten.
Lime	857	$Ca+SO_4$	60+236=296	2·90	2·96 Naumann; 2·93 Karsten.
Magnesia	759	$Mg+SO_4$	40+236=276	2·75	2·61 Karsten.
Soda	892	$Na+SO_4$	130+236=366	2·44	2·46 Mohs; 2·63 K.

SULPHATES: SECOND CLASS.

SULPHATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Lead	1895	$Pb+SO_4$	114+186=300	6·32	6·30 Mohs; 6·17 Karst.
Baryta	1458	$Ba+SO_4$	143+186=329	4·43	4·45 Mohs; 4·20 Karst.
Potassa	1091	$K+SO_4$	234+186=420	2·60	2·62 Karst.; 2·66 Kopp.
Strontia	1148	$Sr+SO_4$	108+186=294	3·90	3·95 Breit.; 3·59 Karsten.

CHROMATES AND TUNGSTATES.

CHROMATES and TUNGSTATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Lead	2046	$Pb+CrO_4$	114+228=342	5·98	5·95 Breith.; 6·00 Mohs.
Potassa	1241	$K+CrO_4$	234+228=462	2·69	2·64 Karst.; 2·70 Kopp.
Lead	2877	$Pb+WO_4$	114+244=358	8·04	8·0 Gmel.; 8·1 Leonh.
Lime	1839	$Ca+WO_4$	60+244=304	6·05	6·04 Kars.; 6·03 Meiss.

CHLORIDES: FIRST CLASS.

CHLORIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Lead	1736	$Pb+Cl$	114+196=310	5·60	5·68, 5·80 Karsten; 5·24, 5·34 Monro.
Silver............	1794	$Ag+Cl$	130+196=326	5·50	5·50, 5·57 Karsten; 5·55 Boul.; 5·13 Herap.
Barium	1299	$Ba+Cl$	143+196=339	3·83	3·86 Boul.; 3·70 Karst.
Sodium	733	$Na+Cl$	130+196=326	2·25	2·26 Mohs; 2·15 Kopp; 2·08 Karsten.

CHLORIDES: SECOND CLASS.

CHLORIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Copper..........	1234	$2Cu+Cl$	$88+245=333$	3·70	3·68 Karsten.
Mercury	1708	$Hg+Cl$	$93+245=338$	5·05	5·14 Gmel.; 5·43 Boul.; 5·40 Karsten.
	2974	$2Hg+Cl$	$186+245=431$	6·90	6·99 Karsten; 6·71 Herapath; 7·14 Boullay.
Ammonium	669	$Am+Cl$	$218+245=463$	1·44	1·45 Watson; 1·50 Kopp; 1·53 Mohs.
Calcium.........	698	$Ca+Cl$	$60+245=305$	2·29	2·21, 2·27 Boullay; 1·92 Karsten.
Potassium......	932	$R+Cl$	$234+245=479$	1·94	1·94 Kopp; 1·92 Karsten.
Strontium......	989	$Sn+Cl$	$108+245=353$	2·80	2·80 Karsten.

In explaining the specific gravity of oxides, it is necessary to make three assumptions for the specific volume of oxygen. In the first small class of oxides, the oxygen is contained with the atomic volume 16; in the second and large class, with the atomic volume 32; and, in the third class, with the atomic volume 64. The metals are supposed to retain their primitive atomic volumes.

TABLE III.—*Atomic Volume and Specific Gravity of Oxides.*

FIRST CLASS.

OXIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Antimony.......	1006	$Sb+2O$	$120+32=154$	6·53	6·53 Boullay; 6·70 Karst.
Chromium......	1003	$2Cr+3O$	$138+48=186$	5·39	5·21 Wöhler.
Tin................	935	$Sn+2O$	$101+32=133$	7·03	6·96 Mohs; 6·90 Boullay; 6·64 Herapath.

SECOND CLASS.

OXIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity.
Antimony.......	1913	$2Sb+3O$	$240+96=336$	5·69	5·78 Boullay; 5·57 Mohs.
Bismuth.........	2960	$2Bi+3O$	$270+96=366$	8·09	8·17 Karst.; 8·21 Herap.; 8·45 Royer and Dum.
Cadmium	797	$Cd+O$	$81+32=113$	7·05	6·95 Karsten.
Cobalt	1038	$2Co+3O$	$88+96=184$	5·64	5·60 Boullay; 5·32 Herap.
Copper	496	$Cu+O$	$44+32=76$	6·53	6·43 Karst.; 6·13 Boul.; 6·40 Herapath.
Iron..............	978	$2Fe+3O$	$88+96=184$	5·31	5·23 Boullay; 5·25 Mohs.
Lead	1394	$Pb+O$	$114+32=146$	9·55	9·50 Boullay; 9·28 Herap.; 9·21 Karsten.
	1494	$Pb+2O$	$114+64=178$	8·40	8·90 Herap.; 8·92 Karst.
	2889	$2Pb+3O$	$228+96=324$	8·91	8·94 Muschenbroek; 8·60 Karst.; 9·20 Boullay.
Manganese.....	446	$Mn+O$	$44+32—76$	5·87	4·73 Herapath.
Mercury	1366	$Hg+O$	$93+32=125$	10·9	11·0 Boullay; 11·1 Herapath; 11·2 Karsten.
Molybdenum...	799	$Mo+2O$	$69+64=133$	6·01	5·67 Bucholz.
Tin................	835	$Sn+O$	$101+32=133$	6·28	6·67 Herapath.
Titanium	504	$Ti+2O$	$57+64—121$	4·16	4·18 Klaproth; 4·20, 4·25 Breithaupt.
Zinc..............	503	$Zn+O$	$58+32=90$	5·48	5·43 Mohs; 5·60 Boullay; 5·73 Karsten.
Ilmenite.........	942	$\begin{Bmatrix}Fe\\Ti\end{Bmatrix}+3O$	$\begin{Bmatrix}44\\57\end{Bmatrix}+96=197$	4·78	4·73, 4·79 Breithaupt; 4·75, 4·78 Kupffer.

THIRD CLASS.

Oxides.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp. Gr.	Observed Specific Gravity
Copper	892	$2Cu+O$	$88+64=152$	5·87	5·75 Karsten, Boyer and Dumas; 6·05 Herapath.
Mercury	2632	$2Hg+O$	$186+64=250$	10·05	10·69 Herap.; 8·95 Karst.
Molybdenum...	899	$Mo+3O$	$69+192=261$	3·44	3·46 Bergman, Thomson; 3·49 Berzelius.
Silver............	1452	$Ag+O$	$130+64=194$	7·48	7·14 Herapath; 7·25 Boullon; 8·26 Karsten.
Tungsten	1483	$W+3O$	$69+192=261$	5·68	5·27 Herapath; 6·12 Berzelius; 7·14 Karsten.

Dr. Kopp has endeavoured to determine the atomic volume of the constituents of many other classes of compounds. The specific gravity of the compounds of sulphur and arsenic with the metals, of water with oxides and salts, of chlorine with the non-metallic elements, are explained in a similar manner on a small number of suppositions. He also shows with considerable success that in those isomorphous substances, of which the crystalline form is only similar, and not absolutely identical, as the carbonates (p. 140), the observed difference between the atomic volumes corresponds with the difference between the crystalline forms. The variation in the atomic volume is thus manifested by a variation in the crystalline form.

[*See Supplement*, p. 685.]

CHAPTER IV.

CHEMICAL AFFINITY.

In the preceding section, compound bodies have been viewed as already formed, and existing in a state of rest. The arrangement, weights, and other properties of their atoms, have also been examined with the relations and classification of the compounds themselves. But chemistry is more than a descriptive science; for it embraces, in addition to views of composition, the consideration of the action of bodies upon each other, which leads to the formation and destruction of compounds. Certain bodies, when placed in contact, exhibit a proneness to combine with each other, or to undergo decomposition, while others may be mixed most intimately without change. The actual phenomena of combination suggest the idea of peculiar attachments and aversions subsisting between different bodies, and it was in this figurative sense that the term *affinity* was first applied by Boerhaave to a property of matter. A specific attraction between different kinds of matter must be admitted as the cause of combination, and this attraction may be conveniently distinguished as *chemical affinity*.

The particles of a body in the solid or liquid state exhibit an attraction for each other, which is the force of *cohesion*, and even different kinds of matter have often an attraction for each other, which is probably of the same nature, although distinguished as *adhesion*. This force retains bodies in contact which are once placed in sufficient proximity to each other. It is exhibited in the adhesion of two smooth pieces of lead pressed together, or perfectly flat pieces of plate-glass, which sometimes cannot again be separated. The action of glue, wax, mortar, and other cements, in attaching bodies together, depends entirely upon the same force. In detaching glue from the surface of glass, the latter is sometimes injured, and portions of it are torn off by the glue, the adhesive attraction of the two bodies being greater than the cohesion of the glass. The property of water to adhere to solid surfaces and wet them, its imbibition by a sponge, the ascent of liquids in narrow tubes, and other phenomena of capillary attraction, and the rapid diffusion of a drop of oil over the surface of water, are illustrations of the same attraction between a liquid and a solid, and between different liquids. But this kind of attraction is deficient in a character which is never absent in true chemical affinity — *it effects no change in the properties of bodies.* It may bind different kinds of matter together, but it does not alter their nature.

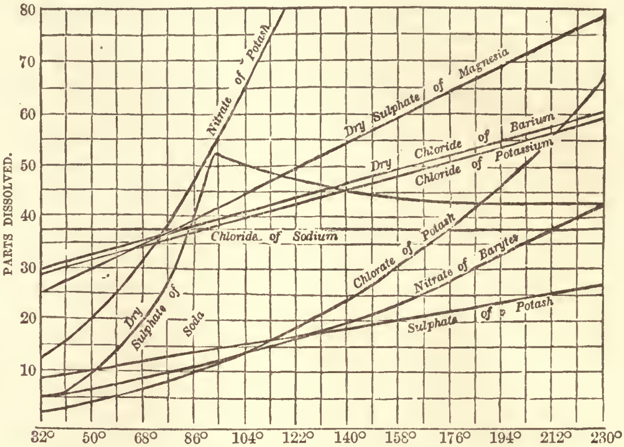
The tendency of different gases to diffuse through each other till a uniform mixture is formed, is another property of matter, — the effect of a force wholly independent of chemical affinity. It is certain that this physical property is not lost in liquids, and that it contributes to that equable diffusion of a salt through a menstruum, which occurs spontaneously, and without agitation to promote it. (Jerichau, in Poggendorff's Annalen, xxxiv. 613; or Dove and Moser's Repertorium der Physik, i. 96, 1837.)

Solution. — The attraction between salt and water, which occasions the solution of the former, differs in several circumstances from the affinity which leads to the production of definite chemical compounds. In solution, combination takes place in indefinite proportions, a certain quantity of common salt dissolving in, or combining with any quantity of water however large; while a certain quantity of water, such as 100 parts, can dissolve any quantity of that salt less than 37 parts, the proportion which saturates it. Water has a constant solvent power for every other soluble salt; but the maximum proportion of salt dissolved, or the saturating quantity, has no relation to the atomic weight of the salt, and indeed varies exceedingly with the temperature of the solvent. The limit to the solubility of a salt seems to be immediately occasioned by its cohesion. Water, in proportion as it takes up salt, has its power to disintegrate and dissolve more of the soluble body gradually diminished; it dissolves the last portions slowly and with difficulty, and at last, when saturated, is incapable of overcoming the cohesion of more salt that may be added to it. The solubility in water of another body in the liquid state is not restrained by cohesion, and is in general unlimited. Thus alcohol, and also soluble salts above the temperature at which they liquefy in their water of crystallization, dissolve in water in any proportion. Generally speaking, also, those salts dissolve in largest quantity which are most fusible, or of which the cohesion is most easily overcome by heat, as the hydrated salts; and among anhydrous salts, the nitrates, chlorates, chlorides, and iodides, which are all remarkable for their fusibility. In this species of combination, bodies are not materially altered in properties; indeed, are little affected except in their cohesion.

The union also between a body and its solvent differs in a marked manner from proper chemical combination in the relation of the bodies to each other which exhibit it. Bodies *combine* chemically with so much the more force as their properties are more opposed, but they *dissolve* the more readily in each other, the more similar their properties. Thus, metals combine with non-metallic bodies, acids with alkalies; but to dissolve a metal, another metal must be used, such as mercury; oxidated bodies dissolve in oxidated solvents, as the salts and acids in water; while liquids which contain much hydrogen are the best solvents of hydrogenated bodies — an oil, for instance, of a fat or a resin; alcohol and ether dissolving the essential oils and most organic principles, but few salts of oxygen acids. The force which produces solution differs, therefore, essentially from chemical affinity in being exerted between analogous particles, in preference to particles which are very unlike; and resembles more, in this respect, the attraction of cohesion.

A more accurate idea of the varying solubility of a salt at different temperatures may be conveyed by a curve constructed to represent it, than by any other means The perpendicular lines in the following diagram, indicate the degrees of temperature which are marked below them, and the horizontal lines, quantities of salt dissolved by 100 parts by weight of water. The proportion of any salt dissolved at a particular temperature may be learned by carrying the eye along the perpendicular line expressing that temperature, till it cuts the curve of the salt, and then horizontally to the column of parts dissolved.[1]

SOLUBILITY OF SALTS IN ONE HUNDRED PARTS OF WATER.



It will be observed that the perpendicular lines advance by 9°, the first being 32°, and the last 230°. The solubility of nitrate of potassa increases from 13 parts in 100 water at 32°, to 80 parts at 118°, or very rapidly with the temperature. Sulphate of soda is seen by the form of its curve to increase in solubility from 5 parts at 32° to 52 parts at 92°, but then to diminish in solubility with farther elevation of temperature. In this salt, sulphate of magnesia and chloride of barium, the solubility is expressed in parts of the anhydrous, and not the hydrated salt. The lines of chloride of barium and chloride of potassium are parallel, showing a remarkable relation between the solubilities of these two salts, which does not appear in any others. The line of chloride of sodium is observed to cut all the lines of temperature at the same height, 100 parts of water dissolving 37 parts of that salt at all temperatures.

Chemical affinity acts only at insensible distances, and has no effect in causing bodies to approach each other which are not in contact, differing in this respect from the attraction of gravitation, which acts at all distances, however great, although with a diminishing force. Hence, the closest approximation of unlike particles is necessary to develope their affinities, and produce combination. Sulphur and copper in mass have no effect upon each other, but if both be in a state of great division, and rubbed together in a mortar, a powerful affinity is brought into play, the bodies themselves disappear, and sulphuret of copper is produced by their union, with the evolution of much heat. The affinity of bodies is, therefore, promoted by every thing which tends to their close approximation; in solids, by their pulverization and intermixture, this attraction residing in the ultimate particles of bodies; in gases, by their spontaneous diffusion through each other, which occasions a more complete intermixture than is attainable by mechanical means; and between liquids, or between a liquid and solid, by the adhesive attraction which liquids possess, which must lead to perfect contact, and also by a disposition of liquid bodies to intermix, of the same physical character as gaseous diffusion. Elevation of temperature has

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[1] An extensive and very careful series of experiments on the solubility of salts in water at different temperatures has been made by M. Poggiale, Ann. de Chim. et de Phys. 3e Sér, T. viii. p. 463; and the *Rapport Annuel* of Berzelius, Paris, 1846, p. 18.

certainly often a specific action in increasing the affinity of two bodies, but it also often acts by producing a perfect contact between them, from the fusion or vaporization of one or both bodies. Hence, no practice is more general to promote the combination of bodies than to heat them together.

If the affinity between two gases is sufficiently great to begin combination, the process is never interrupted, but is continued from the diffusion of the gases through each other till complete, or at least till one of the gases is entirely consumed. Thus, when hydrochloric acid and ammoniacal gases, in equal measures, are introduced into a jar containing at the same time a large quantity of air, the formation of hydrochlorate of ammonia proceeds, the gases appearing to search out each other, till no portion of uncombined gas remains. The combination of two liquids, or of a liquid and a solid, is also facilitated in the same manner by the mobility of the fluid, and proceeds without interruption, unless, perhaps, the product of the combination be solid, and by its formation interpose an obstacle to the contact of the combining bodies. But the affinities of two solids which are not volatile are rarely developed at all, owing to the imperfection of contact. Even the action of very powerful affinities between a solid and a liquid or a gas, is often arrested in the outset from the physical condition of the former. Thus, the affinity between oxygen and lead is certainly considerable, for the metal is rapidly converted into a white oxide when ground to powder and agitated with water in its usual aerated condition; and in the state of extreme division in which lead is obtained by calcining its tartrate in a glass tube, the metal is a pyrophorus, and combines with oxygen when cold with so much avidity as to take fire and burn the moment it is exposed to the air. Iron also, in the spongy and divided state in which it is procured, by reducing the peroxide by means of hydrogen gas at a low red heat, absorbs oxygen with equal avidity at the temperature of the air, and takes fire and burns. But notwithstanding an affinity for oxygen of such intensity, these metals in mass oxidate very slowly in air, particularly lead, which is quickly tarnished indeed, but the thin coating of oxide formed does not penetrate to a sensible depth in the course of several years. The suspension of the oxidation may be partly due to the comparatively small surface which a compact body exposes to air, and which becomes covered by a coat of oxide, and protected from farther change; but partly also to the effect of the conducting power of a considerable mass of metal in preventing the elevation of temperature consequent upon the oxidation of its surface. For metals oxidate with increased facility at a high temperature, such as the lead pyrophorus quickly attains from the oxidation of the great surface which it exposes, compared with its weight. The heat from the oxidation of the superficial particles of the compact metal, however, is not accumulated, but carried off and dissipated by the conducting power of the contiguous particles, so that elevation of temperature is effectually repressed. It thus appears that the state of aggregation of a solid may oppose an insuperable bar to the action of a very powerful affinity.

The affinity of two bodies, one or both of which are in the state of gas, is often promoted in an extraordinary manner by the contact of certain solid bodies. Thus, oxygen and hydrogen gases may be mixed and retained for any length of time in that state without exhibiting any affinity for each other, and the gaseous mixture may, indeed, be heated in a glass vessel to any temperature short of redness without showing any disposition to combine. But if a clean plate of platinum be introduced into the cold mixture, the gases in contact with the metallic surface instantly unite and form water; other portions of the mixture come then in contact with the platinum, and combine successively under its influence, so that a large quantity of the gaseous mixture may be quickly united. The temperature of the platinum also rises, from the heat evolved by the combination occurring at its surface, and the influence of the metal increasing with its temperature, combination proceeds at an accelerated rate, till the platinum becoming red hot, may cause the combination to extend to a distance from it, by kindling the gaseous mixture. Platinum acts in this manner with greatest energy when in a highly divided state, as in the form of spongy platinum, owing to the greater surface exposed, and the rapidity with which it is heated. The metal itself contributes no element to the water formed, and is in no respect altered. It is an action of the metallic surface, which must be perfectly clean, and is retarded or altogether prevented by the presence of oily vapours and many other combustible gases, which soil the metallic surface. Mr. Faraday is disposed to refer the action to an adhesive attraction of the gases for the metal, under the influence of which they are condensed and their particles approximated within the sphere of their mutual attraction, so as to combine. This opinion is favoured by the circumstance that the property is not peculiar to platinum, but appears also in other metals, in charcoal, pounded glass, and all other solid bodies; although all of them, except the metals, act only when their temperature is above the boiling point of mercury. But, on the other hand, at low temperatures, the property appears to be confined to a few metals only which resemble platinum in their chemical characters; namely, in having little or no disposition to combine with oxygen gas, and in not undergoing oxidation in the air. The action of platinum may, therefore, be connected with its chemical properties, although in a way which is quite unknown to us. The same metal disposes carbonic oxide gas to combine with oxygen, but much more slowly than hydrogen; and it is remarkable that if the most minute quantity of carbonic oxide be mixed with hydrogen, the oxidation of the latter under the influence of the platinum is arrested, and not resumed till after the carbonic oxide has been slowly oxidated and consumed, which thus takes the precedence of the hydrogen in combining with oxygen. This extraordinary interference of a minute quantity of carbonic oxide gas, which cannot from its nature be supposed to soil the surface of the platinum like a liquefiable vapour, seems to point to a chemical, perhaps to an electrical explanation of the action of the platinum, rather than to the adhesive attraction of the metal. The oxidation of alcohol at the temperature of the air, and also at a low red heat, is promoted in the same manner by contact with platinum.

Order of affinity. — The affinity between bodies appears to be of different degrees of intensity. Lead, for instance, has certainly a greater affinity than silver for oxygen, the oxide of the latter being easily decomposed when heated to redness, while the oxide of the former may be exposed to the most intense heat without losing a particle of oxygen. Again, it may be inferred that potassium has a still greater affinity for oxygen than lead possesses, as we find the oxide of lead easily reduced to the metallic state when heated in contact with charcoal, while potassa is decomposed in the same manner with great difficulty. But the order of affinity is often more strikingly exhibited in the decomposition of a compound by another body. Thus, sulphuretted hydrogen gas is decomposed by iodine, which combines with the hydrogen, forming hydriodic acid, and liberates sulphur. The affinity of iodine for hydrogen is, therefore, greater than that of sulphur for the same body. But hydriodic acid is deprived of its hydrogen by bromine, and hydrobromic acid is formed; and this last is decomposed in its turn by chlorine, and hydrochloric acid produced. It thus appears that the order of the affinity of the elements mentioned *for hydrogen* is, chlorine, bromine, iodine, sulphur. The order of decompositions, in the precipitation of metals by each other from their saline solutions, also indicates the degree of affinity. Thus, from the decomposition of the nitrates of the following metals, the order of their affinity *for nitric acid and oxygen* may be inferred to be as follows: — zinc, lead, copper, mercury, silver; zinc throwing down lead from the nitrate of lead, and all the other metals which follow it; lead throwing down copper; copper, mercury; and mercury, silver; while nitrate of zinc itself is not affected by any other metal, and nitrate of silver is decomposed by all the metals enumerated. Bodies were first thus arranged according to the degree of their affinity for a particular substance, inferred from the order of their decompositions, by Geoffroy and Bergman, and tables of affinity constructed, of which the following is an example: —

Order of Affinity of the Alkalies and Earths for Sulphuric Acid.

Baryta.
Strontia.
Potassa.
Soda.
Lime.
Ammonia.
Magnesia.

Baryta is capable of taking sulphuric acid from strontia, potassa, and every other base which follows it in the table, — the experiment being made upon sulphates of these bases dissolved in water; while sulphate of baryta is not decomposed by any other base. Lime separates ammonia and magnesia from sulphuric acid, but has no effect upon the sulphates of soda, potassa, strontia, and baryta; and in the same manner any other base decomposes the sulphates of the bases below it in the column, but has no effect upon those above it. Tables of this kind, when accurately constructed, may convey much valuable information of a practical kind, but it is never to be forgotten that they are strictly tables of the order of decomposition and of the comparative force or order of affinity in one set of conditions only. This will appear by examining how far decomposition is affected by accessory circumstances in a few cases.

Circumstances which affect the order of decomposition. — Volatility in a body promotes its separation from others which are more fixed, and consequently facilitates the decomposition of compounds into which the volatile body enters. Hence, by the agency of heat, water is separated from hydrated salts; ammonia, from its combinations with a fixed acid, such as the phosphoric; and a volatile acid from many of its salts: as sulphuric acid from the sulphate of iron, carbonic acid from the carbonate of lime, &c. Ammonia decomposes hydrochlorate of morphia at a low temperature, but, on the other hand, morphia decomposes the hydrochlorate of ammonia at the boiling point of water, and liberates ammonia, owing to the volatility of that body. The fixed acids, such as the silicic and phosphoric, disengage in the same way at a high temperature those acids which are generally reputed most powerful, and by which silicates and phosphates are decomposed with facility at a low temperature. Many such cases might be adduced in which the order of decomposition is reversed by a change of temperature. The volatility of one of its constituents must, therefore, be considered an element of instability in a compound.

Decomposition from unequal volatility is, of course, checked by pressure, and promoted by its removal and by every thing which favours the escape of vapour; such as the presence of an atmosphere of a different sort into which the volatile constituent may evaporate. Carbonate of lime is decomposed easily at a red heat, provided a current of air or of steam is passing over it which may carry off the carbonic acid gas, but the decomposition ceases when the carbonate is surrounded by an atmosphere of its own gas; and the carbonate may even be heated to fusion, in the lower part of a crucible, without decomposition. Here the occurrence of decomposition depends entirely upon the existence of a foreign atmosphere into which carbonic acid can diffuse. Nitrates of alumina, and peroxide of iron in solution, are decomposed by the spontaneous evaporation of their acid, even at the temperature of the air; and so is an alkaline bicarbonate when in solution, but not when dry. A change in the composition of the gaseous atmosphere may affect the order of decomposition, as in the following cases: —

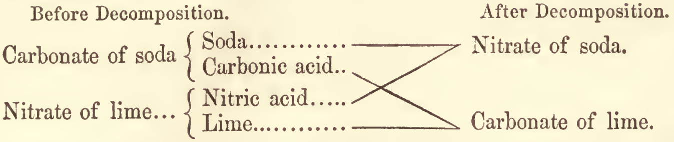
When steam is passed over iron at a red heat, a portion of it is decomposed, oxide of iron being formed and hydrogen gas evolved. From this experiment it might be inferred that the affinity of iron for oxygen is greater than that of hydrogen. But let a stream of hydrogen gas be conducted over oxide of iron at the very same temperature, and water is formed, while the oxide of iron is reduced to the metallic state. Here the hydrogen appears to have the greater affinity for oxygen. But the result is obviously connected with the relative proportion between the hydrogen and steam which are at once in contact with the metal and its oxide at a red heat. When steam is in excess, water is decomposed, but when hydrogen is in excess, oxide of iron is decomposed; and why? because the excess of steam in the first case is an atmosphere into which hydrogen can diffuse, and the disengagement of that gas is therefore favoured; but in the second case the atmosphere is principally hydrogen, and represses the evolution of more hydrogen, but facilitates that of steam. The affinity of iron and hydrogen for oxygen at the temperature of the experiment is so nearly balanced, that the one affinity prevails over the other, according as there is a proper atmosphere into which the gaseous product of its action may diffuse. This affords an intelligible instance of the influence of mass or quantity of material, in promoting a chemical change; the steam or the hydrogen, as it preponderates, exerting a specific influence, in the capacity of a gaseous atmosphere.

The remarkable decomposition of alcohol by sulphuric acid, which affords ether, is another similar illustration of decomposition depending upon volatility, and affected by changes in the nature of the atmosphere into which evaporation takes place. Alcohol or the hydrate of ether is added in a gradual manner to sulphuric acid somewhat diluted, and heated to 280°. In these circumstances, the double sulphate of ether and water is formed; water, which was previously combined as a base to the acid, being displaced by ether, and set free together with the water of the alcohol. The first effect of the reaction, therefore, is the disengagement of watery vapour, and the creation of an atmosphere of that substance which tends to check its farther evolution. But the existence of such an atmosphere offers a facility for the evaporation of ether, which accordingly escapes from combination with the acid and continues to be replaced by the water, the affinity of sulphuric acid for water and for ether being nearly equal, till ether forms such a proportion of the gaseous atmosphere as to check its own evolution, and to favour the evolution of watery vapour. Then the sulphate of ether comes in its turn to be decomposed as before, and ether evolved. Hence, both ether and water distil over in this process, the evolution of one of these bodies favouring the separation and disengagement of the other. In this description, the evolution of water and ether are for the sake of perspicuity supposed to alternate, but it is evident that the result of such an action will be the simultaneous evolution of the two vapours in a certain constant relation to each other.

Influence of insolubility. — The great proportion of chemical reactions which we witness are exhibited by bodies dissolved in water or some other menstruum, and are affected to a great extent by the relations of themselves and their products to their solvent. Thus carbonate of potassa dissolved in water is decomposed by acetic acid, and carbonic acid evolved, the affinity of the acetic acid prevailing over that of the carbonic acid for potassa. But if a stream of carbonic acid gas be sent through acetate of potassa dissolved in alcohol, acetic acid is displaced, or the carbonic acid prevails, apparently from the insolubility of the carbonate of potassa in alcohol. The insolubility of a body appears to depend upon the cohesive attraction of its particles, and such decompositions may therefore be ascribed to the prevalence of that force.

Formation of compounds by substitution. — It is remarkable that compounds are in general more easily formed by substitution, than by the direct union of their constituents; indeed, many compounds can be formed only in that manner. Carbonic acid is not absorbed by anhydrous lime, but readily by the hydrate of lime, the water of which is displaced in the formation of the carbonate. In the same manner, ether, although a strong base, does not combine directly with acids, but the salts of ether are derived from its hydrate or alcohol, by the substitution of an acid for the water of the alcohol. In all the cases, likewise, in which hydrogen is evolved during the solution of a metal in a hydrated acid, a simple substitution of the metal for hydrogen occurs.

Combination takes place with the greatest facility of all when *double decomposition* can occur. Thus carbonate of lime is instantly formed and precipitated, when carbonate of soda is added to nitrate of lime, nitrate of soda being formed at the same time and remaining in solution.



Here a double substitution occurs, lime being substituted for soda in the carbonate, and soda for lime in the nitrate. Such reactions may therefore be truly described as double substitutions as well as double decompositions. They are most commonly observed on mixing two binary compounds or two salts. But reactions of the same nature may occur between compounds of a higher order, such as double salts, and new compounds be thus produced, which cannot be formed by the direct union of their constituents. Thus the two salts, sulphate of zinc and sulphate of soda, when simply dissolved together, at the ordinary temperature, always crystallize apart, and do not combine. But the double sulphate of zinc and soda is formed on mixing strong solutions of sulphate of zinc and bisulphate of soda, and separates by crystallization; the sulphate of water with constitutional water (hydrated acid of sp. gr. 1·78) being produced at the same time, and remaining in solution. The reaction which occurs may be thus expressed:

Before Decomposition. After Decomposition.

$$\left.\begin{array}{l} HO,\ SO_3+(NaO,\ SO_3) \\ ZnO,\ SO_3+(HO) \end{array}\right\} = \left\{\begin{array}{l} HO,\ SO_3+HO \\ ZnO,\ SO_3+NaO,\ SO_3 \end{array}\right.$$

in which the constituents of both salts before decomposition inclosed in brackets, are found to have exchanged places after decomposition, without any other change in the original salts.[1] The double sulphate of lime and soda can be formed artificially only in circumstances which are somewhat similar. It is produced on adding sulphate of soda to acetate of lime, the sulphate of lime, as it then precipitates, carrying down sulphate of soda in the place of constitutional water (Liebig).

Different hydrates of the same body, such as peroxide of tin, differ sensibly in properties, and afford different compounds with acids, unquestionably because these compounds are formed by substitution. The constant formation of phosphates containing one, two, or three atoms of base, on neutralising the corresponding hydrates of phosphoric acid with a fixed base, likewise illustrates in a striking manner the derivation of compounds, on this principle. Many insoluble substances, such as the earth silica, possess a larger proportion of water, when newly precipitated, than they retain afterwards, and in that high state of hydration they may exhibit affinities for certain bodies which do not appear in other circumstances. Hydrated silica dissolves in water at the moment of its separation from a caustic alkali; and alumina dissolves readily in ammonia, when produced in contact with that substance by the oxidation of aluminum. The usual disposition to enter into combination, which silica and alumina then exhibit, is generally ascribed to their being in the *nascent state;* a body at the moment of its formation and liberation, in consequence of a decomposition, being, it is supposed, in a favourable condition to enter anew into combination. But their degree of hydration in the nascent state may be the real cause of their superior aptitude to combine.

Double decompositions take place without the great evolution of heat which often accompanies the direct combination of two bodies, and with an apparent facility or absence of effort, as if the combinations were just balanced by the decompositions which occur at the same time. It is, perhaps, from this cause that the result of double decomposition is so much affected by circumstances, particularly by the insolubility of one of the compounds. For it is a general law, to which there is no excep-

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[1] On Water as a Constituent of Sulphates, Phil. Mag. 3d series, vol. vi. p. 417.

tion, that two soluble salts cannot be mixed without the occurrence of decomposition, if one of the products that may be formed is an insoluble salt. On mixing carbonate of soda and nitrate of lime, the decomposition seems to be determined entirely by the insolubility of the carbonate of lime, which precipitates. When sulphate of soda and nitrate of potassa are mixed, no visible change occurs, and it is doubtful whether the salts act upon each other, but if the mixed solution be concentrated, decomposition occurs, and sulphate of potassa separates by crystallization owing to its inferior solubility.

It may sometimes be proved that double decomposition occurs on mixing soluble salts, although no precipitation supervenes. Thus, on mixing strong solutions of sulphate of copper and chloride of sodium, the colour of the solution changes from blue to green, which indicates the formation of chloride of copper and consequently that of sulphate of soda also. Now it is known that hydrochloric acid will displace sulphuric acid from the sulphate of copper at the temperature of the experiment, while sulphuric acid will, on the other hand, displace hydrochloric from chloride of sodium. It hence appears that in the preceding double decomposition, those acids and bases unite which have the strongest affinity for each other, and the same thing may happen on mixing other salts. But where the order of the affinities for each other of the acids and bases is unknown, the occurrence of any change upon mixing salts, or the extent to which the change proceeds, is entirely matter of conjecture.

It was the opinion of Berthollet, founded principally upon the phenomena of the double decompositions of salts, that decompositions are at all times dependent upon accidental circumstances, such as the volatility or insolubility of the product, and never result from the prevalence of certain affinities over others; and consequently that in accounting for such changes, the consideration of affinity may be neglected. He supposed that when a portion of base is presented at once to two acids, it is divided equally between them, or in the proportion of the quantities of the two acids, and that one acid can come to possess the base exclusively, only when it forms a volatile or an insoluble compound with that body, and thereby withdraws it from the solution, and from the influence of the other acid. His doctrine will be most easily explained by applying it to a particular case, and expressing it in the language of the atomic theory. The reaction between sulphuric acid and nitrate of potassa is supposed to be as follows. On mixing eight atoms of the acid with the same number of atoms of the salt, the latter immediately undergoes partial decomposition, its base being equally shared between the two acids which are present in equal quantities; and a state of statical equilibrium is attained in which the bodies in contact are —

(*a*) Four atoms sulphate of potassa.
Four atoms nitrate of potassa.
Four atoms sulphuric acid.
Four atoms nitric acid.

The nitrate of potassa, it is supposed, is decomposed to the extent stated, and no farther, however long the contact is protracted. But let the whole of the free nitric acid now be distilled off by the application of heat to the mixture, and a second partition of the potassa of the remaining nitrate of potassa is the consequence; the free sulphuric acid decomposing the salt till the proportion of the two acids uncombined in the mixture is again equal, when a state of equilibrium is attained. The mixture then consists of —

(*b*) Six atoms sulphate of potassa.
Two atoms nitrate of potassa.
Two atoms sulphuric acid.
Two atoms nitric acid.

On removing the free nitric acid as before, a third partition of the potassa of the remaining nitrate of potassa between the two acids on the same principle takes place, of which the result is —

(*c*) Seven atoms sulphate of potassa.
One atom nitrate of potassa.
One atom sulphuric acid.
One atom nitric acid.

The proportion of the two acids free being always the same. The repeated application of heat, by removing the free nitric acid, will cause the sulphuric to be again in excess, which will necessitate a new partition of the potassa of the remaining nitrate of potassa, till at last the entire separation of the nitric acid will be effected, and the fixed product of the decomposition be—

(*d*) Eight atoms sulphate of potassa.

Here the affinity of the sulphuric and nitric acids for potassa is supposed to be equal; and the complete decomposition of the nitrate of potassa by the former acid, which takes place, is ascribed to the volatility of the latter acid, which, by occasioning its removal in proportion as it is liberated, causes the fixed sulphuric acid to be ever in excess.

Complete decompositions in which the precipitation of an insoluble substance occurs, were explained by Berthollet in the same manner. On adding a portion of baryta to sulphate of soda, the baryta decomposes the salt, and acquires sulphuric acid, till that acid is divided between the two bases in the proportion in which they are present, and at this point decomposition would cease, were it not that the whole sulphate of baryta formed is removed by precipitation. But a new formation of that salt is the necessary consequence of that equable partition of the acid between the two bases in contact with it, which is the condition of equilibrium; and the new product precipitating, more and more of it is formed, till the sulphate of soda is entirely decomposed, and its sulphuric acid removed by an equivalent of baryta.

According to these views of Berthollet, no decomposition should be complete unless the product be volatile or insoluble, as in the cases instanced. But such a conclusion is not consistent with observation, as it can be shown that a body may be separated completely from a compound, and supplanted by another body, although none of the products is removed by the operation of either of the causes specified, but all continue in solution and in contact with each other. Thus the salt borax, which is a biborate of soda, is entirely decomposed by the addition to its solution of a quantity of sulphuric acid not more than equivalent to its soda, although the liberated boracic acid remains in solution; for the liquid imparts to blue litmus paper a purple or wine-red tint, which indicates free boracic acid, and not that characteristic red tint, resembling the red of the skin of the onion, which would inevitably be produced by the most minute quantity of the stronger acid, if free. But if the borax were only decomposed in part in these circumstances, and its soda equally divided between the two acids, then free sulphuric, as well as boracic acid, should be found in the solution. The complete decomposition of the salt can be accounted for in no way but by ascribing it to the higher affinity of sulphuric acid for soda, than that of boracic acid for the same base.

According to the same views, on mixing together two neutral salts containing different acids and bases, and which do not precipitate each other, each acid should combine with both bases, so as to occasion the formation of four salts. Again, four salts, of which the acids and bases are all dissimilar, should react upon each other in such a way as to produce sixteen salts, each acid acquiring a portion of the four bases; and certain acids and bases, dissolved together in certain proportions, could have but one arrangement in which they would remain in equilibrio. Hence the salts in a mineral water would be ascertained by determining the acids and bases present, and supposing all the bases proportionally divided among the acids. But this conclusion is inconsistent with a fact observed in the preparation of factitious mineral waters, namely, that their taste depends not only on the nature of the salts, but also upon the order in which they are added. (Dr. Struve, of Dresden.) Before we can determine how the acids and bases are arranged in a mineral water, or what salts it contains, it may therefore be necessary to know the history of its formation. Instead of supposing the bases equally distributed among the acids in mixed saline solutions, it is now more generally assumed that the strongest base may be exclusively in possession of the strongest acid, and the weaker bases be united with the weaker acids; a mode of viewing their composition which agrees best with the medical qualities of mineral waters. It thus appears that the doctrines of Berthollet, by which the resulting actions between bodies in contact are made to depend upon their relative quantities or masses, and the physical properties of the products of their combination, to the entire exclusion of the agency of proper affinities between the bodies, cannot be admitted as a true representation of the actual phenomena of combination. [*See Supplement*, p. 730.]

CATALYSIS, OR DECOMPOSITION BY CONTACT.

An interesting class of decompositions has of late attracted considerable attention, which, as they cannot be accounted for on the ordinary laws of chemical affinity, have been referred by Berzelius to a new power, or rather new form of the force of chemical affinity, which he has distinguished as the *Catalytic force*, and the effect of its action as *Catalysis* (from κατα, downwards, and λυω, I unloosen). A body in which this power resides, resolves others into new compounds, merely by contact with them, or by an action of presence, as it has been termed, without gaining or losing anything itself. Thus an acid converts a solution of starch (at a certain temperature), first into gum and then into sugar of grapes, although no combination takes place between the elements of the acid and those of the starch, the acid being found free, and undiminished in quantity, after effecting the change. The same mutations are produced in a more remarkable manner by the presence of a minute quantity of a vegetable principle, *diastase*, allied in its general properties to gluten, which appears in the germination of barley and other seeds, and converts their starch into sugar and gum, which, being soluble, form the sap that rises into the germ, and nourishes the plant. This example of the action of a catalytic power in an organic secretion is probably not the only one in the animal and vegetable kingdoms, for it is not unlikely that it is by the action of such a force that very different substances are obtained from the same crude material by different organs. In animals, this crude material, which is the blood, flows in the uninterrupted vessels, and gives rise to all the different secretions; such as milk, bile, urine, &c., without the presence of any foreign body which could form new combinations. A beautiful instance of an action of catalysis was traced by Liebig and Wöhler in the chemical changes which the bitter almond exhibits. The application of heat and water to the almond, by giving solubility to its emulsin or albuminous principle, enables it to act upon an associated principle, amygdalin, of a neutral character, which then furnishes bodies so unlike itself as the volatile oil of almonds, hydrocyanic and formic acids. The action of yeast in fermentation is a more familiar illustration of a similar power. The presence of that substance, although insoluble, is sufficient to cause the resolution of sugar into carbonic acid gas and alcohol, a decomposition which can be effected by no other known means. Changes of this kind, although most frequent in organic compounds, are not confined to them. The binoxide of hydrogen is a body of which the elements are held together by a very slight affinity. It is not decomposed by acids, but alkalies give its elements a tendency to separate, slow effervescence occurring with the disengagement of oxygen, and water being formed. Nor do soluble substances alone produce this effect; other organic and inorganic bodies, also — such as manganese, silver, platinum, gold, fibrin, &c., which are perfectly insoluble — exert a similar power. The decomposition, in these instances, takes place by the mere presence of the foreign body, and without the smallest quantity of it entering into the new compound; for the most minute researches have failed in discovering the slightest alteration in the foreign body itself. The liquid persulphide of hydrogen, and a solution of the nitrosulphate of ammonia of Pelouze, are decomposed in the same way, and by contact of nearly all the substances which act upon peroxide of hydrogen. One remarkable difference, indeed, is observable, namely, that alkalies impart stability to nitrosulphate of ammonia, while acids decompose it, or the reverse of what happens with both the binoxide and bisulphide of hydrogen (Phil. Mag. 3d Series, vol. x. p. 489).

The phenomena referred to catalysis are of a recondite nature, and much in need of elucidation. The influence of platinum, formerly noticed, in disposing hydrogen and oxygen to unite, is probably connected with the catalytic power of the same metal, but is at present equally inexplicable. It would be unphilosophical to rest satisfied by referring such phenomena to a force of the existence of which we have no evidence. The doctrine of catalysis must be viewed in no other light than as a convenient fiction, by which we are enabled to class together a number of decompositions not provided for in the theory of chemical affinity, as at present understood, but which, it is to be expected, will receive their explanation from new investigations. It is a provisional hypothesis, like the doctrine of isomerism, for which the occasion will cease as the science advances.

SECTION II. — CHEMICAL POLARITY.

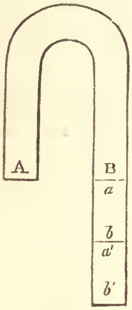
Illustrations from magnetical polarity. — The ideas of induction and polarity, which now play so important a part in physical theories, were originally suggested by the phenomena of magnetism, which still afford the best experimental illustrations of them. A bar magnet exhibits attractive power which is not possessed in an equal degree by every particle composing the bar, but is chiefly localized in two points at or near its extremities. The powers, too, residing at these points are not one and the same, or similar, but different, indeed contrary, in their nature; and are distinguished by the different names of Austral magnetism and Boreal magnetism. The opposition in the mode of action of these powers is so perfect, that they completely negative or neutralize each other when residing in the same particle of matter in equal quantity or degree, as they are supposed really to exist in iron before it is magnetized; and they only signalize their presence when displaced and separated to a distance from each other, as they are in a magnet. A body possessing any such powers residing in it, which are not general but local, and not the same but opposite, is said (in the most general sense) to possess *polarity*.

In the theory of magnetism, it is found necessary to consider a magnet as composed of minute indivisible particles or filaments of iron, each of which has individually the properties of a separate magnet. The displacement or separation of the two attractive powers takes place only within these small particles, which are called the magnetic elements, and must be supposed so minute that they may be the ultimate particles or atoms themselves of the iron. A magnetic bar may, therefore, be represented as composed of minute portions, *a b* in fig. 60 representing one such portion; the right hand extremities of each of which possess one species of magnetism, and the left hand extremities the other. The unshaded ends being supposed to possess austral, and the shaded ends boreal magnetism, then the ends of the bar itself, of which these sides of the elementary magnets form the faces, possess respectively austral and boreal magnetism, and are the austral and boreal poles of the magnet. Such, then, is the polar condition of a bar of iron possessing magnetism, of which the attractive and repulsive powers residing at the extremities are the results. Of the existence of such a structure the breaking of a magnet into two or more parts affords a proof, for it forms as many complete mag-

Fig. 60.

nets as there are parts, new poles appearing at all the fractured extremities. A magnetic element, it is to be remembered, is itself insecable, like a chemical atom, so that the division must take place between magnetic elements.

Fig. 61.



When to the boreal pole B of a magnet (fig. 61), which may be of the horse-shoe form, a piece of soft iron, *a b*, wholly destitute of magnetic powers, is presented, a similar displacement of the magnetic forces of its elements occurs as in the magnet itself; or *a b* becomes a magnet by induction, and may attract and induce magnetism in a second bar *a' b'*; both of which continue magnetic so long as the first remains in the same position, and under the influence of A B. These induced magnets must have the same polar molecular structure as the original magnet, but their magnetism is only temporary, and is immediately lost when they are removed from the permanent magnet. The displacement of the magnetisms in these induced magnets commences at the extremity *a* of *a b*, in contact with B, which extremity has the opposite magnetism of B, (the different kinds of magnetism being mutually attractive,) and is the austral pole of *a b;* and *b* is its boreal pole. Of *a' b'*, again, the upper extremity *a'* in contact with *b'* is the austral, and the lower extremity *b'* the boreal pole, or *b* and *b'* have the same kind of magnetic power as the pole B of the original magnet, from which they are dependent. A third bar of soft iron placed at *b'* is likewise polarized, and the series of induced magnets may be still farther extended, but the attractive powers developed in the different members of the series become less and less with their distance from the pole B of the original magnet.

Fig. 62.

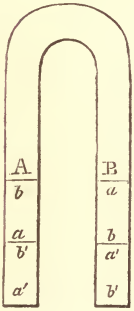
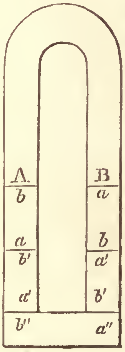
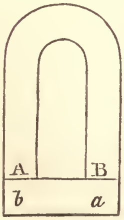


Fig. 63.



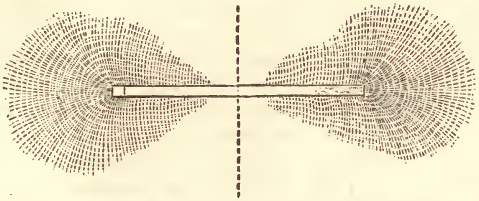
A similar set of bars may be connected with A (fig. 62), which become temporary magnets also according to the same law, the lower extremities of this set being austral. On now uniting the lower extremities of both sets by another bar of soft iron *a'' b''*, (fig. 63), either set renders *a'' b''* a magnet, having its austral pole at *a''* and its boreal pole at *b''*; and acting together, they communicate a degree of magnetism to the uniting bar greater than either set possessed before they were united. By this connexion, also, the inductive actions of each set of bars are brought to bear upon the other, and the attractive forces at all their poles are thereby greatly increased. In the most favourable conditions as to the size and connexion of the temporary magnets with relation to the primary magnet, each of the former, however numerous, acquires powers equal to those of the original magnet. This general enhancement of power in the induced magnets has been acquired, therefore, by completing the circle of them between A and B.

Fig. 64.



It is also important to observe, with a view to the future application of the remark, that a single bar of soft iron, or *lifter*, as *b a*, (fig. 64), connecting the poles of a magnet A B, not only acquires at *b* and *a* equal though opposite powers to the contiguous poles of the magnet, but also reacts by induction on these poles themselves in a gradual manner, and increases their magnetism. The original magnetic forces of A and B are therefore increased, by the opportunity to act inductively, which the connecting bar affords them. The threads of steel filings which are taken up by a magnet, (see figure 65) illustrate the inductive action of magnetism, for each grain of steel is a complete magnet, and the threads a series of connected magnets. It will be observed also that these threads diverge from each other; because, while unlike poles are in contact in each thread, which attract, like poles

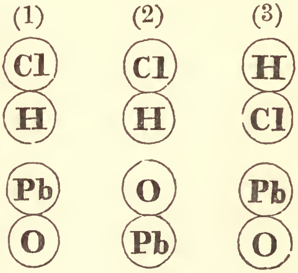
FIG. 65

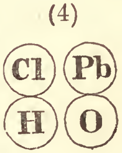


are in contact of adjoining threads which repel. This repulsion of polar chains by each other, there will be occasion again to refer to.

Atomic representation of a double decomposition.—Chemical polarity, although less adapted for exhibition, is still more simple than magnetic polarity in its nature, while it is of a more fundamental character, and appears to be the basis of all other polarities whatever. In a binary compound,—such as chloride of potassium,—there reside two attractive powers, opposite in their nature; namely, the halogenous affinity of the salt-radical chlorine, and the basylous affinity of the metal potassium. The atomic theory gives form to the molecule of chloride of potassium: one atom, Cl, being the seat of the halogenous, chlorous, or negative affinity (as we shall also call it); and the other atom, K, the seat of the basylous or positive affinity. A binary saline molecule is thus entirely similar to a magnetic element. We have to deal with two affinities only,—the chlorous and basylous. Atoms possessing different affinities attract each other; while atoms possessing the same affinity repel each other.

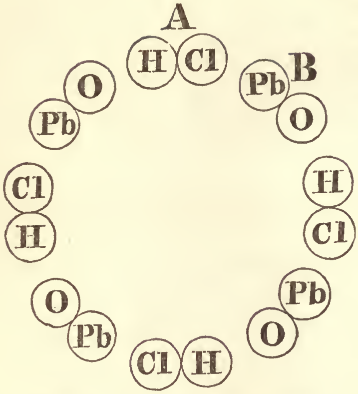
The two binary compounds, hydrochloric acid (chloride of hydrogen) and oxide of lead, when brought into contact, mutually decompose each other, forming chloride of lead and water: $H\,Cl$ and $Pb\,O = Pb\,Cl$ and $H\,O$. At the instant of acting upon each other, the two compound molecules must have a certain relative position. Under (1), the basylous hydrogen of the hydrochloric acid is presented to the basylous lead of the oxide of lead, atoms which repel each other. In (2) and (3), on the contrary, a basylous atom of one molecule is presented to a halogenous atom in the other, H to O in (2), and Cl to Pb in (3). These are attractive pairs; but, before they can enter into new combinations, they must be released from the atoms with which they are already combined; which can be effected in (4), the only disposition of the polar molecules in which both attractive poles are together, and the actual decompositions and combinations possible: Cl is in contact with Pb at the same time that H is in contact with O, allowing the simultaneous formation of Pb Cl and H O. This is no more than the expression of a double decomposition in the language of the atomic theory.





It is further to be observed, that, in the original polar molecules (4), although approximation and combination are promoted by the attraction of the contiguous unlike poles, they are opposed by the mutual repulsion of the like poles; Cl repelling O, and Pb repelling H. This unfavourable influence of the repulsions is reduced to a minimum in the arrangement of several pairs of the hydrochloric acid and oxide of lead molecules to form one circle. In (5), four pairs of the polar molecules are symmetrically placed; HCl alternately with PbO, and the attractive poles of the different molecules together. Affinities tending to a simultaneous formation of chloride of lead and water are equally favoured in this arrangement, as in (4); while the mutual repulsion of the like atoms,—such as the H and Pb, or the Cl and O of the adjoining molecules A and B—is less, as these like atoms are more distant from each other in the circular arrangement. It is obvious that the

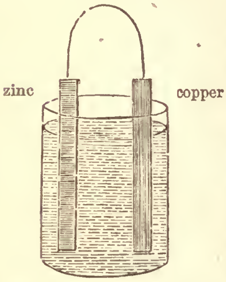
(5)



repelling atoms will be more distant the larger the circle, or the more nearly a segment of it approaches to a straight line. This arrangement of many pairs in a circle, being a condition of equilibrium, is a necessary one, and must take place in all double decompositions occurring in a liquid where the binary molecules are free to move. The formation of such polar circuits explains the ready occurrence of double decompositions; but it is of still more importance, as being the simplest and most intelligible exhibition of a voltaic circle.

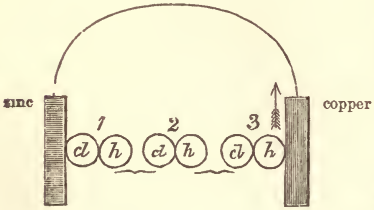
Action of an acid upon two metals in contact. — When a plate of zinc is plunged into hydrochloric acid, a chemical change of a simple nature ensues; the metal dissolves, combining with the chlorine of the acid and displacing its hydrogen, the gas-bubbles of which form upon the zinc plate, increase in size, detach themselves, and rise through the liquor to its surface. The solution of zinc, when effected by its substitution for hydrogen, as in this experiment, is attended by a train of extraordinary phenomena, which become apparent when a second metal, such as copper, silver, or platinum, is placed in the same acid fluid, and allowed to touch the zinc, the second metal being one upon which the fluid exerts no solvent action, or a less action than upon zinc.

Fig. 66.



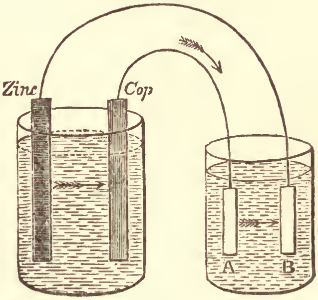
The zinc plate being connected by a metallic wire with a copper plate, as represented in fig. 66, and both dipped together in the hydrochloric acid, the zinc only is acted upon, and dissolves as rapidly as before; but much of the hydrogen gas now appears upon, and is discharged from the surface of the copper plate, and not fron the zinc. The hydrogen, being produced by the solution of the zinc, thus appears to travel through the liquid from that metal to the copper. But no current or movement in the liquid is perceptible, nor any phenomenon whatever to indicate the actual passage of matter through the liquid in that direction. The transference of the hydrogen must take place by the propagation of a decomposition through a chain of particles of hydrochloric acid extending from the zinc to the copper, and may be conceived by the diagram on the margin, in which each pair of associated circles marked *cl* and *h* represents a particle of hydrochloric acid. The chlorine *cl* of particle 1 in contact with the zinc combining with that metal, its hydrogen *h* combines, the moment it is set free, with the chlorine of particle 2, as indicated by the connecting bracket below, and liberates the hydrogen of that particle, which hydrogen forthwith combines with the chlorine of particle 3, and so on through a series of particles of any extent till the decomposition reaches the copper plate, when the last liberated atom of hydrogen (that of particle 3, in the diagram) not having hydrochloric acid to act upon, is evolved and rises as gas in contact with the copper plate.

Fig. 67.



It is to be observed that this succession of decompositions and recombinations leading to the discharge of the hydrogen at the copper, does not occur at all unless that plate be in metallic connexion with the zinc, by means of a wire, as in the figure, or by the plates themselves touching without or within the acid fluid. This would seem to indicate that while the decomposition travels from the zinc to the copper through the acid, some force or influence is propagated at the same time through the wire, from the copper back again to the zinc. That something does pass through the wire in these circumstances is proved by its being heated, and by its temporary assumption of certain electrical and magnetic properties. Whether anything material does pass, or it is merely a vibration or vibratory impulse, or a certain induced condition that is propagated through the molecules of the wire, of which the electrical appearances are the effects, cannot be determined with certainty. But a power to effect decomposition, the same in kind as that occurring in the acid jar, and which acts in the same sense or direction, is propagated through the wire, and appears to be fundamental to all the other phenomena.

Fig. 68.



Let the wire, supposed to be of platinum, connecting the zinc and copper plates, be divided in the middle, and the extremities A and B of the portions attached to the copper and zinc plates respectively be flattened into small plates, and then dipped at a little distance from each other in a second vessel containing hydriodic acid. Iodine will soon appear at A, although that element is incapable of combining with the substance of the platinum, and hydrogen gas will appear at B. If the connecting wire and the small plates A and B were of zinc or of copper, the hydriodic acid would be decomposed precisely in the same manner, but the iodine as it reached A would unite with the metal and form an iodide. Supposing a decomposing force to have originated in the zinc plate, and to have circulated through the hydrochloric acid in the jar to the copper plate, and onwards through the wires and the hydriodic acid back to the zinc, as indicated by the direction of the arrows, then the hydrogen of the hydriodic acid has followed the same course, and been discharged against the metallic surface to which the arrow points.

The solution of the zinc in hydrochloric acid which developes these powers, acting at a distance, is not itself impeded, but on the contrary is promoted by exerting such an influence: for, placed alone in the acid, that metal scarcely dissolves at all, if pure and uncontaminated with other metals, or if its surface has been silvered with mercury; but it dissolves with rapidity when a copper plate is associated with it in the same jar, in the manner described. Hence the decomposing power which appears between A and B cannot be viewed as actually a portion of that which causes the solution of the zinc in the hydrochloric acid, for that force has suffered no diminution in its own proper sphere of action.

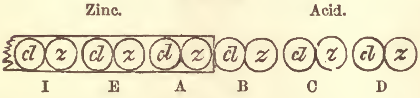
This combination of metals and fluids is known as the *simple voltaic circle.*

To explain the phenomena of the voltaic circle, the existence of a substantial principle, the electric fluid, has been assumed, of such a nature that it is readily communicable to matter, and capable of circulating through the voltaic arrangement, carrying with it peculiar attractive and repulsive forces which occasion the decompositions observed. A vehicle was thus created for the chemical affinity which is found to circulate. But it is generally allowed that this form of the electrical hypothesis has not received support from observations of a recent date, particularly from the great discoveries of Mr. Faraday, which have completely altered the aspect of this department of science, and suggest a very different interpretation of the phenomena. All electrical phenomena whatever are found to involve the presence of matter, or there is no evidence of the independent existence of electricity apart from matter; so that these phenomena may really be exhibitions of the inherent properties of matter. The idea of anything like a circulation of electricity through the voltaic circle appears to be abandoned. Electrical induction, by which certain forces are propagated to a distance, is found to be always an action of contiguous particles upon each other, in which it is unnecessary to suppose that any thing passes from particle to particle, or is taken from one particle and added to another. The change which a particle undergoes takes place within itself, and it is looked upon as a temporary development of different powers in different points of the same particle. The doctrine of polarity has thus come to be introduced into the discussion of electrical phenomena.[1]

One reason for retaining the theory of an electric fluid or fluids is, that it affords the means of expressing in distinct terms those strictly physical laws which are reputed electrical; and for many purposes such an hypothesis is unquestionably useful, if not absolutely necessary; but it has nothing to recommend it in the description of the chemical phenomena of the voltaic circle. These admit of a perfectly intelligible statement, when viewed as an exhibition of ordinary chemical affinity, acting in particular circumstances, without any electrical hypothesis.

Polarity of the arrangement.—It is to be assumed that the zinc and hydrochloric acid are both composed of particles, or molecules, which are susceptible of a polar condition. Of hydrochloric acid, the chemical atom is the polar molecule, and it therefore consists of an atom of chlorine and an atom of hydrogen associated together. The polar molecule of zinc may be supposed, for a reason which will afterwards appear, to consist of a pair likewise of associated atoms, which, however, are in this body both of the same element. The powers appearing in a polar molecule of zinc and of hydrochloric acid are the same. One pole of each molecule has the basylous attraction, or affinity, which is characteristic of zinc, or *zincous* attraction, and may be called the zincous pole; while the other has the halogenous attraction, or affinity, which is characteristic of chlorine, or *chlorous* attraction, and may be called the chlorous pole.

Fig. 69.



Zinc and acid in contact may therefore be represented (fig. 69) by trains of associated pairs of atoms. In the molecule of hydrochloric acid B, which is next the zinc, the chlorine atom forms the chlorous pole, and is turned towards the zinc, the fluidity of the acid allowing its molecule to take that position, which may be indicated by inscribing *cl* in the circle which represents the chlorine atom. The other atom of the molecule B, or the hydrogen, is the opposite, or zincous pole, and is marked *z*. Of the two atoms forming the polar molecule A of the zinc, the exterior atom which is in contact with the acid has thereby zincous attraction developed in it, and becomes the zincous pole, while the interior becomes the chlorous pole, as indicated in both by the inscribed letters. This polar condition of the zinc must be supposed the necessary and immediate consequence of its contact with the polar acid.

But each of these particles throws a train of particles of its own kind into a similar state of polarity: A, the contiguous particles E and I of the zinc, and B, the contiguous particles C and D of the acid. For *cl* of A becoming a chlorous pole, developes near it in an opposite, or zincous pole in *z* of E, and a chlorous pole in *cl*, the more remote extremity of E; in the same manner as the austral pole of a magnet developes, by induction, a boreal and austral pole in a piece of soft iron applied to it. And as the induced magnet, thus formed, will react upon a second piece of iron, and render it also magnetic, so the polarized particle E renders I

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[1] For Mr. Faraday's views, the eleventh and subsequent series of his Researches, in the Philosophical Transactions for 1836, and the following years, may be referred to. He has 'avoured the scientific world with a reprint of the whole series: Faraday's Experimental Researches in Electricity: R. and J. E. Taylor, London, 1839. The subject is also systematically treated in the work of the late Professor Daniell, entitled an Introduction to the 'tudy of Chemical Philosophy, which may be consulted with advantage.

similarly polar. The polar arrangement of the particles C and D of the acid is produced by B in the same manner. But as in a series of induced magnets (fig. 61, page 188), the magnetism acquired diminishes with the distance from the pole of the original magnet, so in trains of chemically polarized molecules, such as A, E, I and B, C, D, the amount of polarity developed in each molecule will diminish with the distance from the sources of induction A and B; I being polarized to a less degree than E, and D than C.

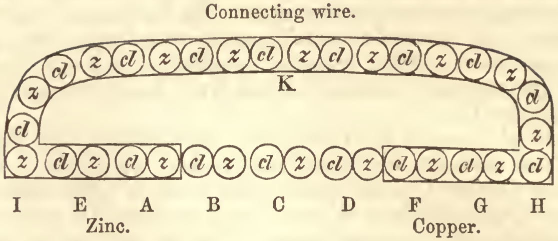
In the electrical theory of the voltaic circle as modified by Mr. Faraday, the zinc and hydrochloric acid are equally supposed to have a polarizable molecule. The polarity is also developed in these molecules by their approximation or contact. The molecule of hydrochloric acid is supposed to contain the positive and negative electricities, which possess contrary powers, like the two magnetisms, and are in combination and neutralize each other, in the non-polar condition of the molecule. But the contact of zinc causes the separation of the two electricities in the acid molecule, its atom of chlorine next the zinc becoming negative, and its atom of hydrogen positive. The electricities of the zinc molecule are separated at the same time, the side of the molecule next the acid becoming positive, and the distant side negative. The positive and negative sides of the two different molecules are thus in contact, the different electricities, like the different magnetisms, attracting each other. Hence, one side of each molecule is said to be positive instead of zincous, and the other side to be negative instead of chlorous. Polarity of the molecule is supposed in both views, but on one view the polar forces are the two electricities, on the other two chemical affinities. The difference between the two views is little more than nominal, for in both the same powers and properties are ascribed to the acting forces. The electricities are supposed to be the cause of the chemical affinities, but it may with equal justice be assumed that chemical affinities are the cause of the phenomena reputed electrical. One set of forces only is necessary for the explanation of the phenomena of combination, and the question is, whether are these forces electrical or chemical? Shall electricity supersede chemical affinity, or chemical affinity supersede electricity? If the electricities should be retained, in discussing the voltaic circle, their names might well be changed, the positive called zincous electricity, and the negative chlorous electricity, which express (as will appear more clearly afterwards), the nature of the chemical affinities with which these electricities are invested, and of which they are indeed constituted the sole depositories. The propagation of the effects to a distance is supposed to take place by the polarization of chains of molecules, on the electrical as well as chemical theory of the voltaic circle; so that the explanations which follow, although expressed in the language of the chemical theory, are the same in substance as those which are given on the electrical theory as now understood.

If the attractions of the respective zincous and chlorous poles of A and B which are in contact, rise to a certain point, the atom *z* of A is detached from the mass of metal, and combines with the atom *cl* of B, which last atom is disengaged at the same time from its hydrogen. Chloride of zinc is produced and dissolves in the liquid, while hydrogen is disengaged and rises from the surface of the metal; or we have the ordinary circumstances of the solution of an isolated mass of zinc in hydrochloric acid.

SIMPLE VOLTAIC CIRCLE.

Circle with the connecting wire unbroken.—When the zinc is pure, or its surface amalgamated with mercury, the zincous and chlorous attractions of the touching poles of A and B are not sufficiently intense to produce these effects, and combination does not occur. Let a copper plate F G H (fig. 70), be then introduced into the acid, and connected by a metallic wire H K I with the zinc. The particles of the acid assume chlorous and zincous poles as before; so also do those of the zinc, and the chain of polar molecules is now continued through the zinc and wire to the

Fig. 70.



copper, the exterior particle F of which, it will be observed, comes thereby to present a chlorous pole to the acid. The contiguous particle D of acid is thus exposed to a second induction from the chlorous polarity of the copper, which increases the zincous polarity of the side of D next F, and, therefore, co-operates in enhancing the polar conditions already assumed by the chain of acid particles extending between the two metals. An endless chain or circle of polar molecules symmetrically arranged is thus formed, such as exists in a magnet of which the poles are united by a lifter, in which every particle in the chain has its own polar condition elevated by induction, and at the same time does itself react upon and elevate the polar condition of every other particle in the chain. The result of this is that the primary attraction of the zinc atom *z* of A, for the chlorine, *cl* of the hydrochloric acid B, is increased, and attains that degree of intensity at which the resistance to the impending combination is overcome, and the *z* and *cl* of A and B unite. But in a circle of polar molecules, in which the condition of any one molecule determines and is determined by that of every other, the intensity of the polar condition is necessarily the same in every element of the circle. The chemical polarity, therefore, of the other particles forming the chain, must increase to an equal degree as with A and B, when the circle is completed, and the same change must now occur in all of them that has occurred in A and B. The pole of B next C is intensely zincous, while that of C next B is intensely chlorous, whence the chlorine and hydrogen *cl* and *z* of these two particles combine together. At the same time, and for the same reason, the hydrogen *z* of C unites with the chlorine *cl* of D; and so on, through a chain of particles of hydrochloric acid of any length, till the copper is reached, when the last acid particle, D in the figure, yields its hydrogen *z* to the chlorous pole of the copper *cl*. But *the hydrogen not being capable of combining permanently with the copper, is liberated as gas upon the surface of that metal.*

Some internal change of a similar character appears to take place in the chain of polarized molecules extending through the metals themselves—a series of molecular detachments and re-attachments, among the atoms of their polar molecules, like the decompositions and recompositions in the acid, causing evolution of heat and other phenomena, generally reputed electrical, which the zinc and copper plates and the connecting wire exhibit.

Amalgamation of the zinc plate.—The polar molecule of the metals has been assumed to contain two atoms (like that of the acid), with the view of assimilating these intestine changes in the solid to those occurring in the fluid portion of the voltaic circuit, and also because it appears to account for the advantage of amalgamating the zinc surface. In the amalgamated plate, it is not zinc itself, but a chemical combination of mercury and zinc, which is presented to the acid, in which mercury is the negative element, and which might, therefore, be called a hydrargyride of zinc. That combination likewise is *fluid.* It must constitute the polar molecule, which will then consist of an atom of mercury as chlorous pole, and an atom of zinc as zincous pole, and not of two atoms of zinc. Such metallic molecules being capable of movement from their fluidity will place themselves, in forming a polar chain, with their unlike poles together, as the fluid acid particles arrange themselves. So that in an amalgam of zinc, of which A, E, and I, are polar molecules (fig. 70), all the atoms marked *cl* are mercury, and those marked *z* are zinc. It thus follows that, when by contact with an acid the amalgam is polarized, it presents a face of zinc only to the acid. If the mercury were exposed to the acid, that metal would completely derange the result, acting locally like a copper plate, as will afterwards be explained. The previous combination of the zinc (with mercury) likewise prevents that metal from yielding easily to the chlorine of hydrochloric acid; and the zinc of the amalgam is, therefore, not dissolved, till the affinities are enhanced by the introduction of a copper plate into the acid, and the formation of a voltaic circle.

It would thus appear that zinc, associated with copper, dissolves more readily in the acid than when alone, because the attraction or affinity of the zinc for chlorine is increased by the completion of a circle of similarly polar molecules, in the same manner as the magnetic intensity at one of the poles of a magnet is increased on completing the circle of similarly polarized elements, by connecting that pole by means of soft iron with the other pole (Fig. 64, page 188).

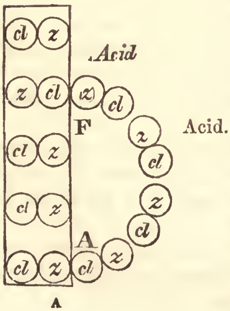
Although the terms of the electrical hypothesis are at present avoided, still it will be convenient to denominate the zinc, being the metal which dissolves in the acid, the active or *positive* metal, and the copper, which does not dissolve, the inactive or *negative* metal of the voltaic circle.

Looking to the condition of the two connected metals in the acid, it will be observed that the surface of the zinc presented to the acid has zincous affinity, or is zinco-polar, but the surface of the copper presented to the acid has, on the contrary, chlorous affinity, or is chloro-polar. Such a condition of the copper is necessary to the propagation of the induction; and the advantage of copper or platinum as the negative metal in a voltaic arrangement depends upon there being little or no impediment to either of these metals assuming the chlorous condition, that can arise from the peculiar affinity of the metals named for the chlorine of the acid; an affinity which tends to cause them to be superficially zincous instead of chlorous. If the second metal were zinc, the surface of it would be disposed to dissolve in the acid, and becoming on that account zincous, would induce a polarization in the intermediate acid in an opposite sense from that induced by the first plate of zinc; which counter polarizing actions would mutually neutralize each other. The acid between the two zinc plates would be like a piece of iron connecting two like magnetic poles, which itself is not then polarized.

But if one of the two zinc plates were less disposed to dissolve in the acid than the other, from the physical condition of its surface, from the acid being weaker there, or from any other cause, then the plate so situated might become negative to the other, and a voltaic circle of weak power be established, in which both metals were zinc.

Impurity of the zinc.—If zinc is alone in the acid, and every superficial particle of the metal equally disposed dissolve, then the zinc everywhere exposes a surface in a state of zincous polarity; and a polar circle in the liquid, starting from one particle of the zinc and returning upon another, cannot be established, as this requires that a part of the zinc surface be chlorous. But if the zinc contains on its surface a single particle of copper, a chlorous pole is created, upon which an inductive circle starting from an adjoining particle of zinc, A, (fig. 71), and passing through the liquid, may return as shown in the figure. It is the formation of such circles that causes impure zinc, which is contaminated by other metals, to dissolve so much more quickly in an acid than the pure metal. Why such circles are not formed when the positive metal in combination with the zinc is mercury, which forms a fluid alloy, has already been accounted for; and the nature of the evil which might otherwise attend the amalgamation of the zinc is now evident.

Fig. 71.



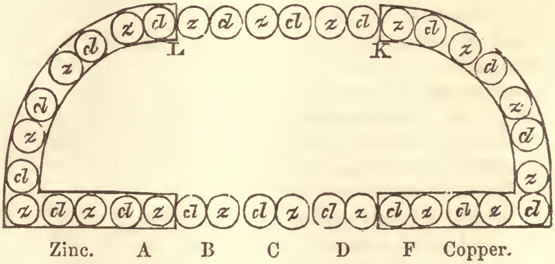
The whole chain of polar molecules in the voltaic circle admits of a natural division into two segments, the acid or liquid segment B C D (fig. 70), and the metallic segment, A K F, each of which has a pair of poles, the unlike poles of the two segments being opposed te each other. The pole at B of the acid portion is chlorous, and is opposed to the zincous pole at A of the metallic segment; while the pole of the liquid segment at D is zincous, and is opposed to the chlorous pole or the metallic segment at F. The distribution of polarity in these two segments is, therefore, the same as in two magnets with their unlike or attracting poles in contact.

Such, then, is the action of affinity by induction, which the mere introduction of zinc and copper in contact into the same acid liquid is sufficient to develope, and which accounts for the discharge of the hydrogen upon the surface of the copper in such an arrangement, the remarkable phenomenon by a description of which this subject was introduced.

Circle with the connecting wire broken.—It remains for us to apply the same principles to explain the additional phenomena of the second case described, in which the connecting wire, supposed to be of platinum, between the zinc and copper plates, is divided, and the broken extremities introduced into hydriodic acid (fig. 70, page 194).

Broken at any point, as at K, (Fig. 70), it is evident that if the polarized condition be still sustained, the portion of the metallic segment connected with the copper plate will terminate with a zincous pole at K, and that connected with the zinc with a chlorous pole; which may be indicated respectively by K and L, in fig. 72. When hydriodic acid is interposed between K and L, the breach is repaired by the polarization of a chain of particles of that acid. The extremity K, being zincous, induces chlorous polarity in the side of the hydriodic acid particle which it touches; in consequence of which the iodine atom (the analogue of chlorine) of the hydriodic acid molecule is presented to that pole, and liberated there when decomposition occurs. The extremity L of the zinc or positive metal element is chlorous, and therefore induces zincous polarity in the particle of hydriodic acid which it touches, and hydrogen (the analogue of zinc) is liberated there. The polarity in an induced circle must necessarily be of equal intensity at every point in it, and being sufficient at A to cause the decomposition of the hydrochloric acid, must also decompose the hydriodic acid between K and L; otherwise it is never established at A, nor anywhere else.

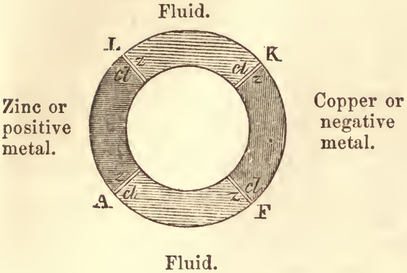
Fig. 72.



In the present arrangement, the voltaic circle is broken into four segments, or has four polar elements, every terminal pole of which is in contact with a pole of a different name; and the whole arrangement may be compared to a circle of four magnets with the attractive poles in contact.

These elements are:—First, the zinc plate or positive metal, A L, of which the end at A, in the hydrochloric acid (fig. 73), has zincous affinity, and the end faced with platinum at L, in the hydriodic acid, chlorous affinity.

Fig. 73.



Secondly, the body of hydrochloric acid, A F, between the zinc and copper plates, of which the surface at A, in contact with the positive metal, has chlorous, and that at F, in contact with the negative metal, zincous affinity.

Thirdly, the copper or negative metal F K, of which the end at F in the hydrochloric acid has chlorous affinity, and that faced with platinum at K in the hydriodic acid, zincous affinity.

And fourthly, the body of hydriodic acid, K L, between the zincous and chlorous poles of the negative and positive metals, of which the surface K, in contact with the negative metal, is chlorous, and the surface L, in contact with the positive metal, zincous.

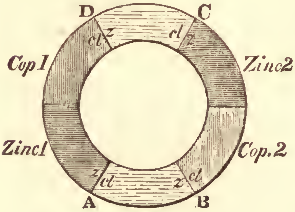
In every voltaic circle employed to produce decomposition these four elements are to be looked for. Hereafter, in adverting to any one of these elements, it will be sufficient to confine our notice to its terminal polarities or affinities, without recurring to the polarized condition of the element itself, upon which its terminal affinities depend.

COMPOUND VOLTAIC CIRCLE.

In both the arrangements described there is only one source of polarizing force, namely, the action between the zinc and acid at A. But a circle of a similar nature may be constructed embracing within itself two or more of such primary sources of polarizing power, and the intensity of the polar condition of the whole circle be thereby greatly increased.

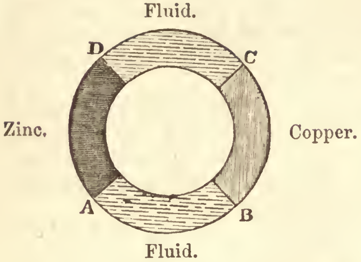
Figure 74 represents such a circle, in which there are two zinc plates, both supposed to be in contact with hydrochloric acid, namely at A and at C, and a copper plate attached to each of these zincs. The polar condition of such a circle will easily be observed. By the contact of the acid and zinc at A, a zincous pole is established there in the first zinc plate, and a chlorous pole in the acid, which are so inscribed in the diagram. These occasion the formation of a chlorous pole at D in the first copper, the united zinc and copper A D forming together one polar element; and a zincous pole at B in the acid, the column A B of acid being the second polar element. The further effect of the induction is to produce a chlorous pole at B in the second copper, of which the corresponding zincous pole is at C, in the second zinc; the united zinc and copper B C forming together a third polar element. And, as a last consequence of the inducing force originating at A, the column of acid between C and D becomes a fourth polar element of the circle, having a chlorous pole at C and a zincous pole at D. Now it will be observed that the chemical affinity between the acid and zinc at C tends to produce the same polar conditions at that point as are already established there from the effect of induction. The extremity of the zinc plate at C is in fact zincous, both primarily and by induction; and the acid in contact with it chlorous, likewise both primarily and by induction; and generally, throughout the whole circle, the polar conditions determined by the second chemical action at C are the same as those determined by the first action at A.

Fig. 74.



In the last arrangement, the inductive actions are in the same direction, and favour each other; but a circle may be constructed in which the inductions, being

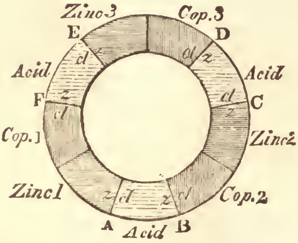
Fig. 75.



in opposite directions, oppose and neutralize each other. Thus if A D (fig. 75) be entirely zinc, both its extremities being exposed to acid, will tend equally to be zincous. In the same way, if B C be entirely copper, the condition of both its extremities will be chlorous, from the action of the acid on the two ends of the zinc; and, consequently, the elements of such a circle could have no polarity.

A circle is represented in fig. 76, containing three sources of polarizing force. It consists of three alternations of copper and zinc symmetrically arranged, and forming three polar elements F A, B C, and D E, with three acid columns between these alternations, which form three additional polar elements, A B, C D, and E F. The number of alternations of copper and zinc with acid may obviously be increased to any extent, and the chemical action of the acid on the zinc in each alternation is found to increase in a marked manner up to the number of 10 or 12 alternations. This increase of the affinity is undoubtedly owing to the favouring inductive action which the chemical actions at the different points have upon each other. Such a compound circle may be compared to a number of magnets disposed in a circle with their attracting poles together, of which each would have its magnetic intensity exalted by induction from all the rest. When such a circle is broken at any point, all chemical action and polarization cease till contact is again made, and the circuit completed. The polarization, too, being the result of a circular induction involving so many lines or chains of particles, cannot, when once established, be more or less at any one point in the circuit than at others. The resulting chemical action must, therefore, be every where equal in the circle, and consequently the same quantity of zinc be dissolved, and hydrogen evolved in each acid.

Fig. 76.



If any metallic element of this compound circle be broken, and a polarizable liquid be interposed between the metallic extremities so as to complete the circuit, decomposition occurs in that liquid as in the simple interrupted circle (fig. 72). But the polarizing influence of the compound circle being of high intensity, more numerous and difficult decompositions are effected by means of it than by the simple circle. The compound voltaic circle is indeed a decomposing instrument of great efficiency.

If, in this arrangement, the position of one of the metals in the series be reversed, so that a zinc is where a copper should be, then, by the action of the acid on that zinc, polarization in the wrong direction is occasioned, which greatly diminishes the general polarity of the circle, reducing it in an arrangement of ten alternations to one-fourth, according to Mr. Daniell.

Voltaic battery.—In the first of the two annexed diagrams (see fig. 77) is represented a compound circle, such as is employed to produce decomposition, and called a voltaic battery, consisting of three acid jars, each of which contains a zinc and copper plate, and which are termed active cells, as they are sources of polarizing power, from the action of acid upon zinc which takes place in them.

In the second diagram (see fig. 78), the same arrangement is repeated, with the addition of a third jar, termed the decomposing cell, which contains any binary polar liquid, with two platinum plates immersed in it. Each copper, it will be seen, is connected by a wire with the following zinc; and, in the first diagram, the copper in the third cell C'' is immediately connected with the zinc in the first cell Z by a wire,

Fig. 77.

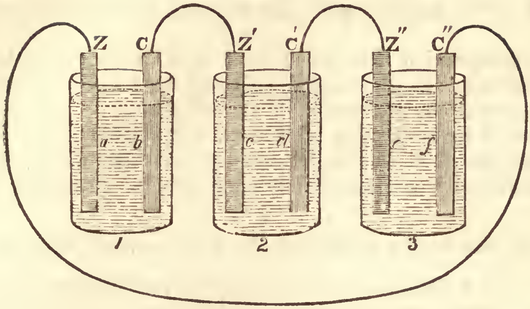
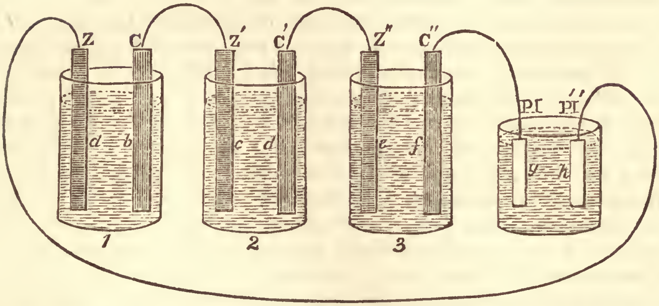


Fig. 78.



and the circuit thus completed. The polar elements in the circle of the first diagram it will be found, are six in number; namely, the three acid columns between the metals in the cells *a b*, *c d*, and *e f;* and the three pairs of zinc and copper plates, each of which pairs forms a single polar element, of which the surface of the zinc is the zincous, and the surface of the copper the chlorous pole. In the second diagram, one of these metallic elements Z C'' is divided, and a polar liquid *g h*, in the cell of decomposition, interposed between the broken extremities Pl and Pl'. To ascertain the polar condition of the extremities, or the terminal platinum plates in the decomposing cell, it is to be observed that Pl' with Z forms one polar element, of which Z being a zincous pole, Pl' must be a chlorous pole. Again, Pl with C'' forms one polar element, of which C'' being a chlorous pole, Pl must be a zincous pole. Now, the platinum plates Pl and Pl', which are thus zincous and chlorous, are disposed in the decomposing cell, in regard to one another,—the first to the left, and the second to the right, as the zincous and chlorous plates (the zinc and copper) also are arranged in the active cells. It will be convenient to distinguish by names the poles which these terminal platinum plates constitute, as they are much more frequently referred to, and of greater consequence than any other poles in the voltaic battery, when used as an instrument of decomposition, as it constantly is. The chlorous plate Pl', which is in connexion with a zinc plate Z, may be called the *chloroid* (like chlorine), and the zincous plate Pl, which is connected with a copper plate C'', may be called the *zincoid* (like zinc),—names which express the virtual properties of each plate, or the particular attractive power and affinity which each of them acquires from its place in the circle.

When hydrochloric acid is the polar liquid interposed between these plates, chlorine is of course attracted by the surface of the zincoid, and discharged there; and hydrogen by the face of the chloroid, and discharged upon that plate. On the electrical hypothesis, the same plates are variously denominated:—

The *zincoid* as the positive pole, the positive electrode, the anode, and the zincode.

The *chloroid* as the negative pole, the negative electrode, the cathode, and the platinode.

The cell of decomposition thus interpolated in the voltaic circle is an obstacle to induction, and reacts on the whole series, reducing the chemical action and evolution of hydrogen in each of the active cells by at least one-third. In that retarding cell itself, the amount of decomposition is necessarily the same as in the other cells. Mr. Daniell found the chemical action reduced to one-tenth in a series of eight active and two such retarding cells; and entirely stopped by three retarding to seven active cells.

OF THE SOLID ELEMENTS OF THE VOLTAIC CIRCLE.

The elements of a Voltaic Circle are obviously of two different kinds—the metals or solid portions, through the substance of which chemical induction is propagated without decomposition; and the liquids in the cells, which yield to the induction and suffer decomposition. In reference to the first, it is to be observed that, as only iron and one or two other metals of the same natural family are susceptible of magnetic polarity, so the susceptibility of chemical polarity which appears in the voltaic battery is not possessed by solids in general, but is confined to the class of bodies to which zinc belongs,—the metals, all of which possess it, with the addition of carbon in the form of charcoal, and certain metallic sulphides, more particularly the sulphide of silver when heated. Weak solutions of the alkaline sulphides, containing an excess of sulphur, also admit of a feeble polarity without undergoing decomposition. The non-metallic elements, with their compounds, the oxides and salts of the metals, are destitute of this power, and cannot, therefore, be used as solid elements of the circle. A body available for this purpose is termed a *conductor* on the electrical hypothesis, a name which may be retained as it is not at variance with the function assigned to the metals in the circle viewed as a chemico-polar arrangement. Two different metals are combined in a circle, one of which is acted on by the liquid, and, therefore, called the active or the positive metal; while the other is not acted upon, and is, therefore, called the inactive or the negative metal; and it has already been stated, that the more easily acted on by the liquid, or the more highly positive the one metal, and the less easily acted upon, or more negative the other metal, the more proper and efficacious is the combination. In the following table several of the metals are arranged in the order in which they appear positive or negative to each other, when acted on by the acid fluids commonly employed in the voltaic battery. Each metal is positive to any one below it in the table, and negative to any one above it.

Most positive.
Potassium.
Sodium.
Manganese.
Zinc.
Cadmium.
Iron.
Nickel.
Cobalt.
Lead.
Tin.
Bismuth.
Copper.
Silver.
Mercury.
Palladium.

Carbon.
Platinum.
Rhodium.
Iridium.
Gold.
Most negative.

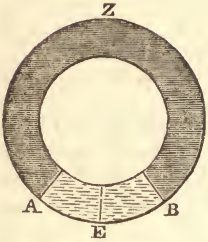
Zinc, which stands high in the list, is the only metal which can be used with advantage in the voltaic battery, as the positive metal. Although closely approaching zinc in the strength of its affinities, iron is ill adapted for the purpose, from the impossibility of amalgamating its surface, the irregularity of its structure, and certain peculiarities of this metal in reference to chemico-polarity. Platinum forms an excellent negative metal, from the weakness of its affinities, and is generally used for the plates in the cell of decomposition. Silver also is highly negative, but copper is the only negative metal which from its cheapness can be used in the construction of active cells of considerable magnitude.

Voltaic protection of metals.—But although the difference between two metals in point of affinity be very small, yet their association in the same acid always gives a decided predominance to the affinity of the more positive, by causing the surface of the other to become chlorous, and therefore wholly inactive in an acid fluid. A negative metal may thus be protected from the solvent action of saline and acid liquids, by association with a more positive metal; iron, for instance, by zinc, as in articles of *galvanized iron*, which are coated with the former metal. The process is analogous to the making of tin-plate. The surface of the iron (generally sheet iron) is first cleaned from all adhering oxide by a dilute acid; then immersed in a weak solution of tin, with fragments of metallic tin, according to the improved practice of Messrs. Morewood and Rogers, by which the iron is covered by a film of tin, to which zinc is capable of adhering more uniformly than to an iron surface. The article so prepared is then passed once through a bath of melted zinc, of which the surface is covered by the fused chloride of zinc and ammonium, to protect the metal from oxidation. It thus acquires a smooth and beautifully crystallized coating of zinc. Copper is protected by either zinc or iron, as was remarkably illustrated in the attempt made by Sir H. Davy to defend the copper sheathing of ships from corrosion in sea-water, by means of his *protectors*. These were small masses of iron or zinc fixed upon the ship's copper, at different points under the water line. They completely answered the purpose of protecting the copper, but unfortunately gave rise to a deposition of earthy matter upon that metal to which barnacles and sea-weeds attached themselves, and thereby diminished the facility of the ship's motion through the water. The more recent substitution, by Mr. Muntz, of an alloy of 60 parts of copper and 40 of zinc, for pure copper, has proved more successful. In acting as a protecting positive metal, zinc necessarily undergoes corrosion, but more slowly than might be expected. On zinced articles which are exposed to the air only, and not immersed in water, a film of suboxide of zinc soon appears, which forms a hard covering, and protects the metal below from further change.

On the other hand, the injurious effect of association with a *negative* metal is often accidentally illustrated, as in the corrosion of the ends of iron railings, which are fixed in their sockets by lead, a more negative metal. In dye-coppers, an iron steam-pipe with a rose of lead or copper is quickly destroyed. Some kinds of cast iron undergo a rapid corrosion, when exposed to sea-water, the carbon acting as a negative body and ultimately remaining in the form of plumbago after all the metal has disappeared.

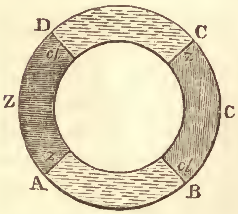
A weak voltaic circle may even be formed of a single positive metal in an acid, as the zinc A B (fig. 79), provided the surfaces of the metal exposed to the acid at A and B are in different conditions as to purity or mechanical structure, and therefore unequally acted upon by the acid; whereupon the part least disposed to dissolve becomes negative to the other. A zinc plate may also be unequally acted on and

Fig. 79.



thrown into a polar state, from the liquid in which it is immersed varying in composition and activity at different points of the metallic surface. A circle may thus be formed of one metal A Z B, with two liquids A E and E B, which merge into each other, and form together one polar element A B.

Fig. 80.



The two metals in a circle have generally been exhibited in metallic contact, and forming together one polar element, but they may be separated, as are the zinc and copper plates A D and C B in the diagram (fig. 80), by two fluids, provided these fluids are such as a strong acid at A B, and as iodide of potassium at D C, the first of which acts very powerfully on zinc, while the other acts very feebly upon that metal (unless associated with copper); so that of the consequent opposing inductions, that originating at A greatly exceeds and overpowers that of D. It is likewise necessary that the fluid D C be of easy decomposition, so as to yield to the polar power of the single circle. In this arrangement, however, it is obvious that the zinc itself forms a complete polar segment, of which A is the zincous, and D the chlorous pole; and the copper also an entire polar segment of which B is the chlorous, and C the zincous pole.

The preceding table exhibits the relation which the metals enumerated assume to each other, in the acid and saline solutions usually employed as exciting fluids. But the relation of any one metal to another is not the same in all exciting fluids. Thus when tin and copper are placed in acid solutions, the former is most rapidly corroded and becomes the positive metal, according to its position in the series, but if they are put into a solution of ammonia which acts most upon the copper, then the latter becomes the positive metal. Copper is positive to lead in strong nitric acid, which oxidizes the former most freely, whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is positive.

LIQUID ELEMENTS OF THE VOLTAIC CIRCLE.

With the view of simplifying the statement of the circular decompositions which occur in the voltaic circle, the exciting fluid has hitherto always been supposed to be hydrochloric acid (chloride of hydrogen), and this compound is a fair type of the class of bodies which possess a polar molecule, and are available for the purpose of bringing these changes into play. The exciting fluid is always a *saline body* in the general sense; that is, a binary compound of a salt-radical or halogen, such as chlorine, with a basyl, such as hydrogen or a metal. The chloride of copper, chloride of sodium, chloride of ammonium, or the chloride of any other basyl, may be substituted for hydrochloric acid, although not all with the same advantage; and the chlorides of basyls may be replaced by their iodides, sulphionides (sulphates), nitrationides (nitrates), and salts of other acids, as exciting fluids, provided they have the condition of liquidity, which gives mobility to their particles, and permits that disposition of them which is assumed in a polar chain. The liquids which yield in the cell of decomposition are of the same nature, possessing always a binary polar molecule, although the liquid which forms the best exciting fluid is not always the most easily decomposed in the decomposing cell.

The positive metal which is exposed to the exciting fluid always acts in one way, displacing the basyl and combining with the halogen of that body; in the manner the zinc has been seen to liberate hydrogen and combine with chlorine, when hydrochloric acid is the exciting fluid. The positive metal is thus substituted for a similar basyl in a pre-existing saline compound. That metal may dissolve in another manner, by uniting directly, for instance, with free chlorine or iodine in solution, but then no polar chain is formed. Particles of chlorine may extend from the zinc to the associated negative metal, but not possessing a binary molecule they have no occasion to throw themselves into a polar chain in order to act upon the zinc, as the molecules of hydrochloric acid require to do in the same circumstances. The particles of these free elements appear to be incapable of that polar condition, having chlorous affinity on one side and zincous on the other, of which both the solid and liquid constituents of the voltaic circle must be susceptible. Judging from the uniformity in composition of exciting liquids, their capacity to form polar chains depends on their consisting of an atom of basyl and an atom of salt-radical, which are respectively the locus of zincous and chlorous affinity or polarity. Such molecules may be looked upon as in a state of tension when forming a part of a polar chain, each about to divide into its chlorous and zincous atoms. Mr. Faraday had established that all exciting liquids are binary compounds of single equivalents of salt-radical and basyl, or *proto-compounds*, such as hydrochloric acid itself, proto-chloride of tin, &c. Other saline bodies which are *per-compounds*, such as bichloride of tin, are not exciting or polar, because, as may be supposed, they are not naturally resolvable into a chlorous and zincous atom, but into a chlorous atom and *another salt;* the bichloride of tin, for instance, into chlorine and proto-chloride of tin. Certain compounds, which are deficient in the saline character and not polarizable, such as chloride of sulphur, and the liquid chlorides of phosphorus and carbon, have been enumerated as exceptions to this rule. None of these bodies, however, is really a proto-compound.

The zinc or positive metal, too, always forms a proto-compound in dissolving, which is a saline body. The order of the chemical changes in the exciting fluid therefore is as follows: — The zinc in decomposing a binary compound and forming a binary compound liberates an atom of its own class; which atom repeats the same actions; supplying at the same time another atom of the same kind to act in the same manner, and that another, from the zinc to the copper plate. The combining bodies are always a basyl and a salt-radical, and therefore only two kinds of attraction or affinity are at work throughout the chain, those of a basyl and a salt-radical, the zincous and chlorous affinities. Hence, in the present subject of chemical polarity, we have to deal with but two attractive forces, the zincous and the chlorous, as in magnetism with but two magnetic forces, the austral and the boreal.

On the electrical hypothesis, a body which is thus decomposed in the active cells, or in the cell of decomposition, is called an *electrolyte* (decomposable by electricity), and this kind of decomposition is distinguished as *electrolysis.* The two elements of an electrolyte, which travel or are transferred in opposite directions, in its decomposition have been named *ions* (from 'ιων, going); the halogen which travels to the positive metal or terminal, the *anion* (going upwards), and the basyl, which is transferred to the negative metal, or terminal, the *cation* (going downwards). Strictly chemical expressions equivalent to the former would be *zincolyte* and *zincolysis*, the decompositions throughout the circle being referred to the affinity of zinc or the positive metal.

The characters of the two constituents of an electrolyte may be shortly noticed. The class of basyl constituents is composed of the metals in their order as positive metals, beginning with potassium, and terminating with mercury, platinum, and the less oxidable metals. Ammonium has a claim to be introduced high in this list, and should probably be accompanied by the analogous basyl of the aniline class of bases and of the vegeto-alkalies, although in respect to the decomposition of their salts in the voltaic circle, we have little precise information. Hydrogen likewise finds a place near copper in this class.

At the head of the halogen constituents of electrolytes may be placed iodine and the other members of the chlorine family. These are followed by the halogens of the sulphates, nitrates, carbonates, acetates, and other oxygen-acid salts. Sulphur must be allowed to follow the last, as the salt-radical of the soluble sulphides, and the lowest place be assigned to oxygen, as the salt-radical of the soluble metallic oxides; of oxide of potassium, for instance, and of water. It is unusual to speak of oxygen as a salt-radical, and of caustic potassa and water as salts, but the binary theory of salts recognizes no essential difference between the chloride, sulphionide, and oxide of a basyl, the oxide being connected with the more highly saline compounds through the sulphide, and the list of salt-radicals forming a continuous descending series from iodine to oxygen.

The facility of decomposition of different electrolytes appears to depend more upon the high place of their salt-radical, than upon the nature of their other constituent. The iodides, for instance, as iodide of potassium and hydriodic acid, are the most easily decomposed of all salts, yielding to the polar influence of the single circle. Then follow the chlorides,—chloride of lead, fused by heat, yielding to a very moderate power. After these the salts of strong oxygen acids, such as sulphates and nitrates either of strong bases, such as potassa and soda, or of weak bases, such as oxide of copper and water (the hydrated acids are such salts). The carbonates and acetates, which have much weaker salt-radicals, are still less easily decomposed, and finally oxides are decomposed with great difficulty. Water itself is polarized with such extreme difficulty, and decomposed when alone to so minute a degree, even by a powerful battery, as long to have left its claim uncertain to be considered an electrolyte, when in a state of purity.

Widely as the more characteristic halogens and basyls differ, still the classes pass by imperceptible gradations into each other, and form portions of one great circular series. Mercury and the more negative metals, although clearly basyls, appear at times to assume the salt-radical relation to the highly positive metals; such a character is evinced in mercury, by the energy with which it unites with sodium and potassium, and by its function in the amalgamated zinc plate of the voltaic circle. So that the salt-radical or basyl character of a body is not absolute, but always relative to certain other bodies.

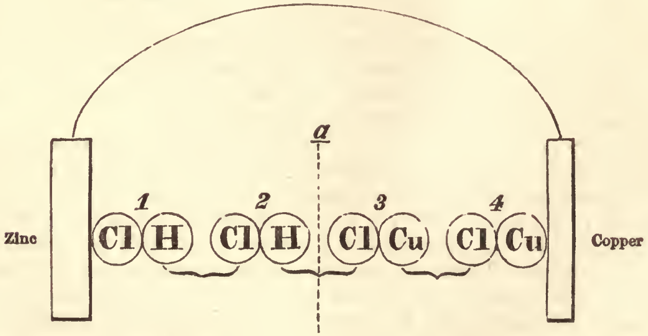
The addition of a salt or acid, even in minute quantity, to water in the cell of decomposition, causes the copious evolution of oxygen and hydrogen gases at the zincoid and chloroid, and is therefore often spoken of as facilitating, by its presence, the decomposition of the water, in some way which cannot be explained. But the phenomena are unattended with difficulty on the binary theory of saline bodies. When sulphate of soda exists in the water of the decomposing cell, it may be sulphionide of sodium which is decomposed, SO_4, the sulphate radical being evolved at the zincoid, and sodium at the chloroid. But the sodium having a strong affinity for oxygen reacts upon the water at the pole, forming soda and liberating hydrogen, which therefore appear together; while SO_4 having, as a high salt-radical, a powerful affinity for hydrogen, likewise decomposes water, and thus evolves oxygen, which, with a free acid, appears at the zincoid. A solution of chloride of sodium is decomposed in the same manner, its elements chlorine and sodium being attracted to the zincoid and chloroid respectively, but neither of these elements appearing as such. Both decompose water, and thus produce oxygen with hydrochloric acid at the zincoid, and soda with hydrogen at the chloroid. It has indeed been ascertained that the polar influence which apparently effects two decompositions in these circumstances, namely, that of water into oxygen and hydrogen, and of a salt into its acid and alkali, is no more in quantity than is necessary to decompose one of these bodies, the circulating power being measured by the quantity of fused chloride of lead decomposed in another part of the circuit (Daniell). There can be little doubt, then, that only one binary compound is immediately decomposed, and that the two sets of products which appear at the terminals are the results of secondary decomposition. Indeed, the decomposition of salts in the voltaic circle is supposed to afford considerable support to the salt-radical theory of these bodies (page 156.)

Certain salts form a polar chain, or conduct, without undergoing decomposition, in a way which cannot at present be explained, particularly the iodide of mercury and fluoride of lead, both fused by heat. According to recent observations of M. Matteucci many other fused salts conduct to a greater extent than is indicated by their decomposition.

Secondary decompositions.—The products of voltaic action are frequently of the secondary character just described, the original products being lost from their reaction upon the liquid in which they are produced, or upon the substance of the metallic terminals. Thus, salts of the vegetable acids often afford carbonic acid, and salts of ammonia nitrogen, instead of oxygen, at the positive terminal or zincoid; the oxygen liberated having reacted upon the combustible constituents of these bodies. Nitrates, again, may afford nitrogen, or nitric oxide, at the negative terminal or chloroid, in consequence of the oxidation of the hydrogen evolved there. The nascent condition of the liberated elements favours such secondary actions. When the zincoid is composed of a positive metal, such as zinc itself or copper, the chlorous element is absorbed there, combining with the metal. The decomposition of a salt is also then much easier, the action of the circle being greatly assisted by the proper affinity of the matter of the zincoid for a chlorous body. Indeed, when two pieces of the same metal communicate by means of one of its salts, the phenomena are the same as if the metallic circuit were complete (Faraday). Insoluble sulphides, chlorides, and other compounds of a positive metal acting as the zincoid, have thus been slowly produced in a single circle with a weak exciting fluid; which products have exhibited distinct crystalline forms, resembling natural minerals, not otherwise producible by art. The hydrogen evolved upon a platinum chloroid, immersed in the solution of a copper or iron salt, may also reduce these metals upon the surface of the platinum, in the form of brilliant octahedral crystals. In the active cells themselves a secondary decomposition is apt to occur, the hydrogen evolved decomposing the salt of zinc which accumulates in the liquid, and occasioning a deposition of that metal upon the copper plate; an occurrence which may determine an opposite polarity, and cause the action of the circle to decline. But on disconnecting the zinc and copper plates, the foreign deposit upon the latter is quickly dissolved off by the acid. The inconvenience of this secondary decomposition in the exciting cells is avoided by dividing the cell into two compartments, by a porous plate of earthenware interposed between the zinc and copper plates. The salt of zinc formed about that metal is prevented from diffusing to the copper, by the diaphragm, although it allows, from its porosity, a continuity of liquid polar molecules between the metals.

Two polar liquids separated by a porous diaphragm.—The liquids on either side of the porous division may also be different, provided they have both a polar molecule. Thus, in fig. 81, the polar chain is composed of molecules of hydrochloric acid, extending from the zinc to the porous division at *a*; and of molecules of chloride of copper, from *a* to the copper plate. When the Cl of molecule 1 unites with zinc, the H of that molecule unites with the Cl of molecule 2 (as indicated by the connecting bracket below), the H of molecule 2 with the Cl of molecule 3, the Cu of molecule 3 with the Cl of molecule 4, and the Cu of this molecule, being the last

FIG. 81.



in the chain, is deposited upon the copper plate. Dilute sulphuric acid, in contact with an amalgamated zinc plate, and the same acid fluid saturated with sulphate of copper, in contact with the copper plate, are a combination of fluids of most frequent application. In such an arrangement, the formation of small gas bubbles upon the negative plate, which makes its contact with the acid fluid imperfect, is avoided; and the surface of that plate is kept clean and entirely metallic by the constant deposition of fresh copper upon it. The copper is deposited in a coherent state, and forms a plate, which may be stripped off from the original copper after attaining any desired degree of thickness, — and presents an exact impression of the surface of the latter. In the operation of *electrotyping*, the article to be copied is so placed in a copper solution as the negative plate of a voltaic pair, being first made conducting, if not metallic and already so, by rubbing its surface over with fine plumbago. With a negative plate of platinum, undiluted nitric acid may be used in the place of the acid solution of copper in the last arrangement, with oil of vitriol, diluted with four or five times its bulk of water, about a positive plate of amalgamated zinc. The polar molecules will be, on the binary theory of salts, $NO_6 + H$, in the former, and $SO_4 + H$, in the latter fluid. The hydrogen is also here entirely suppressed at the negative plate, uniting with the fifth equivalent of oxygen in nitric acid to form water, which is attended with the evolution of peroxide of nitrogen, NO_4. The solution of the zinc, with such an arrangement of fluids, appears to give the most intense polarization that can be attained.

Application of the voltaic circle to chemical synthesis. — The liquid in the decomposition cell may be divided by a porous diaphragm placed between the platinum plates, which form the zincoid and the chloroid in a similar manner, and the synthetical results of the voltaic action be had more readily apart from each other. With a solution of chlorate of potassa between the plates, it is found that the oxygen, instead of being evolved at the positive pole as gas, is communicated to the chlorate of potassa there, and converts it into perchlorate (Berzelius). In a solution of chloride of potassium, even when rendered acid by sulphuric acid, chlorate, and afterwards perchlorate of potassa were found at the positive pole (Kolbe). A concentrated solution of chloride of ammonium evolves hydrogen at the negative pole; but neither oxygen nor chlorine at the positive pole. But the surface of the platinum plate representing the latter pole is covered with small, yellow, oily drops of chloride of nitrogen, which, as soon as the two poles are brought into contact, decompose with explosion (Kolbe). A solution of the yellow prussiate of potassa is converted into the red prussiate by the action of the oxygen at the positive pole (Smee). Dr. Kolbe oxidized the cyanide of potassium in the same manner, and converted it into cyanate of potassa, but did not succeed in obtaining a percyanate: nor did he succeed in forming a fluorate of potassa from the fluoride of potassium by the same means (Mem. of the Chem. Soc., vol. iii. p. 287). The decomposition of a concentrated neutral solution of valerianate of potassa in the cold gave a gaseous carbo-hydrogen, C_8H_8, of double the density of olefiant gas, and what appeared to be a new ether, containing C_2H_2 less than amylic ether. Such transformations from the series of one alcohol to that of another are of great importance, and the attaining them by voltaic action highly interesting. Six pairs of Bunsen's carbo-zinc battery were employed in these decompositions, and the action continued for several days (Kolbe, Memoirs of the Chemical Society, vol. iii. p. 378).

Transference of the ions. — With a double diaphragm cell, in which the liquid between the poles was divided into three portions, Messrs. Daniell and Miller were enabled to make some singular observations on the transfer of the ions and their accumulation at the poles. With a neutral salt of the potassium family (such as sulphate of soda), for one equivalent of salt decomposed, half an equivalent of free acid is added to the division of the cell containing the positive pole, and half an equivalent of free alkali to the division containing the negative pole — the amount of transference which the polar decomposition requires: but, with a salt of the magnesian family (such as sulphate of zinc), while the acid travels as usual to the positive pole and accumulates there, no corresponding transference of oxide of zinc takes place in the opposite direction. This seems to imply that water travels, as base, instead of oxide of zinc. All the magnesian salts retain one equivalent of water very strongly; and, in the polar chain, probably assume this water as their base, so as to become equivalent to hydrated acids in solution. In the decomposition of salts of oxide of ammonium, the ammonia also appears passive, and does not move towards the negative pole, although the acid of the salt travels as usual towards the positive pole. The water, which is essential to the salts of oxide of ammonium, appears to be here again, the base which travels; and in a polar chain extending through a salt of ammonia, such as the sulphate of ammonia, we have probably sulphate of water as the polar molecule; the ions being SO_4 and H; not SO_4 and NH_4.[1]

Voltaic endosmose. — It was first observed by Mr. Porrett, that in the decomposition cell, divided into two chambers by a permeable diaphragm of wet bladder or porous earthenware, the liquid tends to pass from the chamber containing the positive terminal plate into that containing the negative terminal, so as to rise at times several inches in the latter above its level in the former (Annals of Philosophy, 1816). This accumulation of liquid at the negative pole is only considerable with liquids of an inferior conducting power, that is, of difficult decomposition, and is greatest in pure water.

The transfer takes place of a large quantity of water with the hydrogen of the negative pole, as if the ions were O on the one side, and H + Water on the other. In a polar molecule, such as this implies, we must have an aggregation of many atoms of water forming one compound polar atom. Let us suppose six atoms of water associated H_6O_6; the polar molecule will be $H_6O_5 + O$, in which H_6O_5 is the basyl, and O the salt-radical. Taking advantage of the graphical representation of such a compound molecule by a polar formula (page 168), in which the letters exhibit the relative position of the constituent atoms, we have —

$$\text{Positive Pole.}\ \left|\ \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ O & O & O & O & O & O \\ \hline H & H & H & H & H & H \end{array}\ \right|\ \text{Negative Pole.}$$

The oxygen 1 is alone attracted by the positive metal or pole with which it is in contact, while hydrogen (1) being so far relieved from the attraction of its own oxygen, comes under the influence of oxygen 2, 3, 4, 5, and 6. As the salt-radical O (1) separates, we have thus the temporary formation of the basylous atom —

$$\frac{O\ \ O\ \ O\ \ O\ \ O}{H\ \ H\ \ H\ \ H\ \ H\ \ H},\ \text{or}\ \frac{O_5}{H_6}.$$

But instead of involving six atoms of water, as in this illustration, the compound polar molecule may embrace hundreds or thousands. It will always be represented by $H_nO_{n-1} + O$; H_nO_{n-1} being the basylous atom which is transferred to the negative pole, and O the salt-radical atom which is transferred to the positive pole. It appears to be by a polarization of this sort that, in bad conductors, mass compensates for conducting power; as in the return current of the electric telegraph through the earth, where the resistance is found to be even less than in the metallic wires; indeed, quite inappreciable.

It is found by Mr. J. Napier that the passage of a salt without decomposition, such as sulphate of copper, from the positive to the negative division of the decomposition cell, may take place independently of the water in which it is dissolved, and to a greater proportional amount (Mem. Chem. Soc. ii. 28). This unequal movement of the salt and water proves that the phenomenon is not simply a flowing of

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[1] Professors Daniell and Miller, "On the Electrolysis of Secondary Compounds," in the Philosophical Transactions, 1844.

the liquid towards the negative pole; and it allows us to suppose that an aggregate polar molecule may be formed of many atoms of a salt, as well as of water. It is only in dilute saline solutions that the voltaic endosmose is perceptible.

VOLTAIC CIRCLES WITHOUT A POSITIVE METAL.

If we dip together into an acid fluid two platinum plates, one clean, and the other coated with a film of zinc or highly positive metal, we have the speedy solution of the positive metal by the usual polar decomposition, and hydrogen transferred to the opposite platinum plate. It appears that hydrogen, sulphur, phosphorus, and various other oxidable substances, will originate a polar decomposition in water or a saline fluid, when associated with platinum, in the same manner as the zinc is in the last experiment; and circles may thus be formed without a positive metal. The non-metallic but oxidable elements enumerated cannot be substituted in mass for zinc or the positive metal, because they are non-conductors; but in the thinnest films they are not so, if we may judge from experiments of this kind, and become quite equivalent to metals. Farther, with chlorine or any other strongly halogenous element dissolved in water, and placed in contact with one of the platinum plates, while the other is clean, we may have a polarisation originating with the chlorine, and causing the transfer of the oxygen or salt-radical of the interposed water, or saline fluid, to the clean platinum. Nothing like this is witnessed in the voltaic combination of two metals; it is equivalent to an action in which the copper or negative metal originated the polarization by its affinity for the hydrogen or basylous constituent of the polar liquid.

1. With hydrogen gas dissolved in the acid fluid of one chamber of the divided cell, and air or oxygen in the other, polarisation occurs on uniting the platinum plates, attended with the oxidation of the hydrogen and disappearance of both gases (Schönbein). Viewing this arrangement as a simple circle, consisting of a liquid and metallic segment (page 194), we have to consider particularly the composition of the terminal polar molecules at either end of the metallic segment — platinum with hydrogen must form the one at the positive pole, and platinum with oxygen the other at the negative pole: —

$$(1) \qquad \begin{array}{ccc} \mathrm{Pt\ H} & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & \mathrm{O\ Pt} \\ - \quad + & \text{acid} & - \quad + \end{array}$$

These are equivalent to the external molecules of the two metals, zinc and copper, in the usual voltaic arrangement, which are composed in that case of two atoms of zinc on the one side, and two atoms of copper on the other (fig. 70, page 194): —

$$(2) \qquad \begin{array}{ccc} \mathrm{Zn\ Zn} & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & \mathrm{Cu\ Cu} \\ - \quad + & \text{acid} & - \quad + \end{array}$$

The peculiar superiority of platinum, as the single metal, in arrangements of the present class, depends upon its strictly intermediate character between basyls and halogens, so that it lends itself to form a polar binary molecule equally with hydrogen or oxygen in (1), — with both basyl and salt-radical.

The intermediate liquid (the acid) must be a binary compound as usual. Here the positive hydrogen combines with the salt-radical of that binary compound, and sends its hydrogen or basyl to the second or opposite plate; while the oxygen at that plate decomposes the binary liquid also, sending back oxygen or salt-radical to the hydrogen of the first plate. There are, therefore, two concurring polarisations in every polar chain, tending to bring about simultaneously the same combinations and decompositions throughout the circle: hydrogen enters into combination on the one side, and oxygen on the other, in one and the same polar chain. The union of concurring primary zincous and chlorous polarisations, exhibited in such an arrangement, offers a new means of increasing polar intensity, entirely different from the multiplication of couples in the compound circle, of which the application will be fully observed afterwards in the nitric acid battery of Mr. Grove. The temporary combination of hydrogen with copper, the former as the basylous and the latter as the halogenous element of one polar molecule, which it is necessary to assume in explaining the circular polarity of the ordinary voltaic circle (page 194), is quite in accordance with the relation of hydrogen to platinum in the present circles.

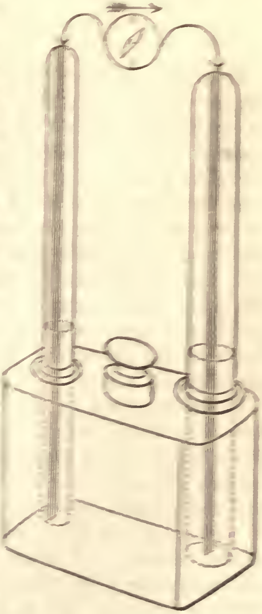
2. A circle of still higher power is formed with chlorine gas, dissolved in the negative chamber, against hydrogen in the positive chamber of the divided cell. Here the terminal polar molecules of the metallic segment are:—

$$(3) \qquad \underset{-\;+}{\mathrm{Pt\,H}} \;\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\; \underset{-\;+}{\mathrm{Cl\,Pt}}$$

3. *Inflammation of mixed hydrogen and oxygen by platinum.*—There is every reason to believe that the remarkable action of clean platinum, both in the form of a plate and of platinum sponge, in disposing a mixture of oxygen and hydrogen in the gaseous state to unite, is the same in nature as its action upon these elements liquefied and in solution in water. In the former, as in the latter case, a polar chain must arrange itself in the platinum mass, of which one terminal molecule is platinide of hydrogen, and the other oxide of platinum (3). A less certain point is, whether the chain is completed by the interposition of a binary molecule of water already formed, between the polar H and O; or these atoms come immediately into contact, and close the circle, without the intervention of any compound polar molecule.

4. *Gas-battery.*—The gas-battery of Mr. Grove belongs to this class of voltaic arrangements. It is essentially an apparatus in which a supply of both negative and positive gas is kept over the liquid at each plate, to supply loss by absorption. A simple circle consists of a bottle (fig. 32), containing a dilute acid, with two tubes filled with oxygen and hydrogen respectively, and placed in two openings in the bottle. The platinum plates contained in these tubes are made rough by adhering reduced spongy platinum, which enables them also to retain the better on their surface a portion of the acid fluid into which they dip. The two plates are connected by a wire above the tubes, which is represented in the figure as carried round a magnetic needle, to obtain evidence of polarization in the wire. Here, as in (2), the gases only act when in contact with the platinum surface and taking a part in the terminal polar molecule, and also when covered by liquid, which is necessary to complete the polar chain between the terminal polar molecules on each side. The gases in the tubes are supplementary, and do not take a part in the polar chain. The modifications of this battery, where, instead of hydrogen gas, sulphur or phosphorus, vaporized in nitrogen gas, or a gaseous hydrocarbon, is placed at the positive pole, are of the same character, and only act by supplying a film of an oxidable body, such as sulphur, or phosphorus, to the surface of the platinum, capable of forming the positive element of a polar molecule with that metal. This, again, must be covered by the binary acid fluid, in order to communicate by a polar chain with the oxygen of the terminal molecule of platinum and oxygen in the negative chamber of the divided cell. (Grove, on the Gas Voltaic Battery: Philosophical Transactions, 1843 and 1845).

Fig. 32.



5. Closely resembling these circles is that in which one of the platinum plates is covered by a film of peroxide of lead or peroxide of manganese. The platinum plate may be so prepared by making it the negative terminal for a short time in a

solution of acetate of lead or of protosulphate of manganese. In an acid fluid, which is capable of dissolving the protoxide of lead or manganese, polarization occurs, the excess of oxygen of the attached peroxide forming with platinum a polar molecule, in which the oxygen is the chlorous element. This decomposes the saline molecule of the acid, or water, causing the transference of the salt-radical or oxygen to the clean platinum plate, where it may be evolved as gas. This most nearly resembles the case with chlorine—water at one platinum plate, which causes the evolution of oxygen at the other platinum plate; the only source of polarizing power in the circle being a chlorous affinity.

6. By much the most powerful voltaic arrangement of this class is that in which one chamber of the divided cell is charged with a solution of sulphide of potassium, and the other chamber with strong nitric acid.[1] Here we have two concurring sources of polarization in one polar chain, namely, the affinity of sulphur for oxygen, tending to transmit hydrogen in one direction, and the easy decomposition of nitric acid into $N\,O_4$ and O, supplying oxygen to the surface of the platinum, which sends a chlorous element in the opposite direction. The terminal polar molecules of the metallic segment of the circle are—

$$(4) \qquad \underset{-\ +}{\mathrm{Pt\ S}} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ \underset{-\ +}{\mathrm{O\ Pt}}$$

With a single pair of plates so charged, water may be decomposed. The action is equally powerful with chlorine substituted for the nitric acid. Such combinations of fluids may be greatly varied: all that is necessary is an oxidable substance at one plate, and an oxidizing substance at the other. In the first class are protosalts of iron, tin and manganese, sulphides, sulphites, hyposulphites; in the second, chlorine, nitric, chromic and manganic acids, and persalts of iron and tin. Taking protoxide of iron against peroxide as an example of these cases, the terminal molecules of the metallic segment may be represented as—

$$(5) \qquad \underset{-\ +}{\mathrm{Pt\ Fe}} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ \underset{-\ +}{\mathrm{O\ Pt}}$$

It is true we have no evidence of the actual separation of the iron or of the oxygen upon the platinum surface; still there is reason to believe such a polarity to be established, assisted by secondary affinities; the oxygen of the protoxide of iron passing over to an adjoining double molecule of protoxide, and converting it into peroxide, to allow the metal to join in a polar molecule with the platinum. At the same time, the peroxide of iron at the negative plate may become protoxide, while its oxygen is engaged in forming a polar molecule with the platinum. But the intensity of polarization with the salts of iron against each other is feeble compared with that of chlorine or nitric acid against an alkaline sulphide. In all these cases the polar circle must be completed by a saline compound in the liquid or liquids, which may serve as the means of connecting the terminal molecules described of the platinum plates, and by metallic polar molecules through the wire connecting the platinum plates.

It was supposed by M. Becquerel that a circle of the present description may be formed in which the affinities are those of an acid for an alkali: the acid and alkaline solutions being separated by porous baked clay, which leaves them in free liquid contact, although their actual mixture proceeds with extreme slowness. Sulphuric acid and potassa, however, are generally admitted to be nearly or altogether incapable of producing this effect, while acids which part readily with oxygen, such as iodic, chloric, chromic, or nitric acid, with an alkali, produce a powerful effect. The polarization may be referred to the oxygen of the acids, in these last cases, at the negative terminal, and is a chlorous affinity. It may possibly be often assisted by

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[1] Mr. A. R. Arnott, on "Some New Cases of Voltaic Action;" Memoirs of the Chem. Soc. i. 142.

minute quantities of ammonia, organic or other oxidizable matter, at the positive terminal in the alkaline solution. (Becquerel, Elements d'Electro-Chimie, 1843).

Theoretical considerations.—The facility with which circular decompositions take place, and the necessity of their occurrence in the action of binary compounds, which was explained under the atomic exhibition of a double decomposition at page 189, are undoubtedly the key to the great stimulus to chemical activity, which the voltaic arrangement affords. Reverting to the original illustration of the action of hydrochloric acid upon zinc, it may be observed that zinc has a strong attraction for chlorine, and would combine at once with that element if the latter were free, without foreign aid of any kind. But with the chlorine of hydrochloric acid the case is different. That chlorine is already combined and strongly retained by its own hydrogen: to enable the chlorine to enter into a new combination we must relieve it from this attraction, by engaging otherwise the affinity of the hydrogen. The contrivance of the voltaic circle is to present another halogen to the hydrogen, and thus divert its affinity from the chlorine—the latter being thereby left free to combine with the zinc. This requires a train of similar decompositions passing round a circle to the zinc, illustrated in diagram 70 of page 194; and which ends in relieving the external combining atom of zinc from the attraction of even the contiguous atom of the same kind; thus dissolving the attraction of aggregation in the metal, and resigning the external atom of zinc entirely to the attraction of the equally relieved chlorine. It is entirely, therefore, because the agent applied to the zinc is a binary compound, and not a free element, that this circular mode of action is necessary.

It is to be remarked in explanation of the facility with which the mutual combinations and decompositions in a circular chain occur, that they do not necessarily consume any power or occasion waste of force. They may be compared to the movement of a nicely balanced beam on its pivot, or the oscillation of a pendulum, in which the motion is equal in two opposite directions, and requires only the minimum of effort to produce it.

Farther, it is not to be supposed that zinc dissolves by a circular action of affinity, only when a negative metal is attached to it, and a voltaic circle purposely constructed. For this positive metal never appears to dissolve in hydrochloric acid in any other manner; the formation of little polar circles in the fluid, starting from one point of the metallic mass and returning upon another, being always required for its solution (page 195). In the solution of zinc, therefore, by a binary saline body, such as hydrochloric acid, the circular or voltaic polarization is the necessary, as well as the most effective mode of action of chemical affinity.

The molecular condition of conductors, such as carbon and the metals, in a voltaic circle, appears to be that of polymeric combination. Their atoms must be feebly basylous and chlorous to each other; the distinction possibly depending upon inequality in their proportions of combined heat, and maintain the relation of combination. Again, many of these binary molecules are associated together like the many similar atoms of carbon, or of hydrogen, which we find associated in the polymeric hydrocarbons. The whole must be held together by their chemical affinities, and the aggregation of the mass be the final resultant of the same attractions. The determination of the polar condition in two metals, by the mere application of heat or cold to their junction, requires the assumption of the sali-molecular structure of metals; and the other proposition, that affinity passes into aggregation, is equally necessary to account for the polar (or electrical) effects which are produced by friction or abrasion, as they appear to extend to the division of chemical molecules.

The cumulative nature of chemical combination is well illustrated in such compounds as the acid hydrates—in dilute sulphuric acid, for instance, where we find an atom of acid uniting with more and more atoms of water, with a decreasing affinity, but without any assignable limit to their number. It is worthy of remark that the acids are bodies with chlorous or negative atoms, and their peculiar affinity in excess. The polar formula for sulphuric acid (page 168) is $\frac{O_3}{S}$; or three negative to one positive atom. By the apposition of a single binary molecule of water, sulphate of water is produced, $\frac{O_3\ O}{S\ H}$, in which the excessive proportion of chlorous atoms and affinity in the compound is in some degree diminished, the formula of the latter presenting four negative to two positive atoms. The apposition of more and more molecules of water is determined by this excess of chlorous affinity, which it tends to neutralize; the constant difference, or excess of two chlorous over the number of basylous atoms, becoming proportionally less with large numbers of added molecules of water. All the magnesian bases appear to assume water to assist in neutralizing their acid in the same manner, and retain one equivalent of this water in general very strongly. In the formation of a polar chain through a solution of a sulphate of this class, we have had reason to suppose that the sulphuric acid applies itself, for the time, to the water rather than the metallic oxide as its base (page 206). The phenomena of voltaic endosmose were also found to favour the idea of the polarization of highly aggregated molecules, in which the binary molecule was represented by a single atom of chlorine or salt-radical, against a single atom of hydrogen or metal associated with a large number of atoms of water, which constituted together the basylous atom. The application of polar formulæ to the explanation of voltaic decompositions of all kinds would, I believe, more correctly express the molecular changes that occur, than the usual assumption of the binary division of the compound body, in an absolute manner, into a basylous atom and a fictitious group forming a halogen body.

GENERAL SUMMARY.

1. In a closed voltaic circle, a certain number of lines or chains of polarized molecules is established, each chain being continuous round the circle. Hence the polar condition of the circle must be every where the same. The same number of particles of exciting fluid are simultaneously polar upon the surface of every zinc plate in the active cells, and also upon the surface of the zincoid in the cell of decomposition, and the consequent chemical change, or decomposition occurring, is of the same amount in all the cells in the same time. This equality in condition and results is essential to a circular polarization, such as exists in the voltaic circle.

The number of polar chains that can be established at the same time in a particular voltaic arrangement, is obviously affected by several circumstances:—

(1) By the size of the zinc plate: the number of particles of zinc that may be simultaneously acted upon by the exciting fluid being directly proportional to the extent of metallic surface exposed.

(2) By the nature and accidental state of the exciting liquid, some electrolytes being more easily acted on by the positive metal than others; while the state of dilution, temperature, and other circumstances, may affect the facility of decomposition of any particular electrolyte.

(3) The adhesion of the gas bubbles of hydrogen to the copper plate, at which they are evolved, interferes much with the action of a battery; partly by reducing the surface of copper in contact with acid, and partly by acting as a zincous element, and originating an opposite polarization in the battery (page 209). By taking up the hydrogen, by means of a solution of sulphate of copper in contact with the copper plate, Mr. Daniell increased the amount of circulating force six times.

(4) The chemical action in a cell is also diminished by increasing the distance from each other in the exciting fluid of the positive and negative metals.

(5) The lines of chemico-polar molecules in the exciting fluid should be repulsive of each other, like lines of magneto-polar elements, as illustrated in the mutual repulsion and divergence of the threads of steel filings which attach themselves to

the pole of a magnet (fig. 65, page 189). That the lines of induction do diverge greatly in the acid, starting from the zinc as a centre, is placed beyond doubt by many experiments of Mr. Daniell. A small ball of zinc suspended in a hollow copper globe filled with acid, is the arrangement in which this divergence is least restrained, and was found to be the most effective form of the voltaic circle. When the copper, too, is a flat plate, and wholly immersed in the acid, the back is found to act as a negative surface, as well as the face directly exposed to the zinc, showing that the lines of induction in the acid expand, and open out from each other, some bending round the edge of the copper plate and terminating their action, after a second flexure, on its opposite side. To collect these diverging lines, the surface of the copper may be increased with advantage to at least four times that of the zinc.

(6) The polar chains of molecules, in the connecting wires and other metallic portions of the circle must be equally repulsive of each other. Hence the small size of the negative plates in the active cells, and of the platinum plates in the cell of decomposition, and the thinness of the connecting wires, are among the circumstances which diminish the number of polar chains that can be established, and impair the general efficiency of a battery.

2. The effect of multiplying the active cells in a battery is not to increase the number of polar chains, or *quantity* of decomposition, but to increase the *intensity* of the induction in each chain; although this increase in intensity generally augments the quantity also, in an indirect manner, by overcoming more or less completely such obstacles to induction as have been enumerated.

3. The intensity of the induction, also, is much greater with some electrolytes than others. Thus a single pair of zinc and platinum plates excited by dilute sulphuric acid, decomposes iodide of potassium, proto-chloride of tin, and fused chloride of silver, but not fused nitre, chloride or iodide of lead, or solution of sulphate of soda. With the addition, however, of a little nitric acid to the sulphuric, the same single circle decomposes all these bodies, and even water itself. Here we have a primary chlorous induction from the oxygen of the nitrous acid, in addition to the basylous induction of the zinc (page 208). The former action also is attended by the suppression of the hydrogen, so that the evolution of that gas upon the negative plate is avoided.

4. The division of the connecting wire, and the separation of its extremities to the most minute distance from each other, is sufficient to stop all induction and the propagation of the polar condition in an arrangement with the usual good conducting fluids. In a powerful voltaic battery consisting of seventy large Daniell cells, no induction was observed to pass when the terminal wires were separated not more than the one-thousandth of an inch, even with the flame of a spirit-lamp or rarefied air between them. Absolute contact of the wires was necessary to establish the circulation. But after contact was made, and the wires were heated to whiteness, they might be separated to a small distance without the induction being interrupted: the space between them was then filled with an arch of dazzling light, containing detached particles of the wire in a state of intense ignition, which were found to proceed from the zincoid to the chloroid, — the former losing matter, and the other acquiring it. So highly fixed a substance as platinum is carried from the one terminal to the other in this manner; but the transference of matter is most remarkable between charcoal points, which may be separated to the greatest distance, and afford the largest and most brilliant arch of flame. A similar, although it may be an excessively minute detachment of matter, is found to accompany the electric spark in all circumstances. Hence, the electric spark always contains matter. In a powerful water battery, however, of a thousand couples, where the conducting power of the liquid is low, good sparks are obtained on approaching the terminals (Gassiot).

5. When terminal wires of a voltaic circle are grasped in the hands, the circuit may be completed by the fluids of the body, provided the battery contains a considerable number of cells, and the induction is of high intensity: the nervous system is then affected, the sensation of the electric shock being experienced.

6. The conducting wire becomes heated precisely in proportion to the number of polar chains established in it, and consequently in proportion to the size of the zinc plate; and this to the same degree from the induction of a single cell as from any number of similar cells. Wires of different metals are unequally heated, according to the resistance which they offer to induction. The following numbers express the heat evolved by the same circulation in different metals, as observed by Mr. Snow Harris:—

	Heat evolved.	Resistance.
Silver	6	1
Copper	6	1
Gold	9	1½
Zinc	18	3
Platinum	30	5
Iron	30	5
Tin	36	6
Lead	72	12
Brass	10	3

The conducting powers of the metals are inversely as these numbers; silver being a better conductor than platinum in the proportion of 5 to 1. The conducting power of all of them is found to be diminished by heat.

7. As a portion of the voltaic circle, the conducting wire acquires extraordinary powers of another kind, which can only be very shortly referred to here, belonging as they properly do to physics.

(1) Another wire placed near and parallel to the conducting wire, has the polar condition of its molecules disturbed, and an induction propagated through it in an opposite direction to that in the conducting wire.

(2) If the conducting wire be twisted in the manner of a corkscrew so as to form a hollow spiral or helix, it will be found in that form to represent a *magnet*, one end of the helix being a north, and the other a south pole; and, if moveable, will arrange itself in the magnetic meridian, under the influence of the earth's magnetism. Its poles are attracted by the unlike poles of an ordinary magnet, and it imparts magnetism to soft iron or steel by induction. Two such helices attract and repel each other by their different poles, like two magnets. Indeed, an ordinary magnet may be viewed as a body having a helical chain of its molecules in a state of permanent chemico-polarity.

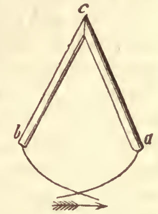
(3) If a bar of soft iron bent into the form of a horse-shoe, with a copper wire twisted spirally round it, be applied like a lifter to the poles of a permanent magnet, at the instant of the soft iron becoming a magnet by induction, the molecules of the spiral become chemico-polar; and when contact is broken with the permanent magnet, and the soft iron ceases to be a magnet, the wire exhibits a polarity the reverse of the former. By a proper arrangement, electric sparks and shocks may be obtained from the wire, while the soft iron included within it is being made and unmade a magnet. The magneto-electric machine is a contrivance for this purpose, and is now coming to supersede the old electric machine, as a source of what is termed electricity of tension. Magnetic and electric effects are thus reciprocally produced from each other.

(4) When the pole of a magnetic needle is placed near the conducting wire, the former neither approaches nor recedes from the latter, but exhibits a disposition *to revolve round it.* The extraordinary and beautiful phenomena of electrical rotation are exhibited in an endless variety of contrivances and experiments. As the magnetic needle is generally supported upon a pivot, it is free to move only in a horizontal plane, and consequently when the conducting wire is held over or under it (the needle being supposed in the magnetic meridian), the poles in beginning to describe circles in opposite directions round the wire, proceed to move to the right and left of it, and thus deviate from the true meridian. The amount of deviation in degrees

is proportional to the quantity of circulating induction, and may be taken to represent it, as is done in a useful instrument, the galvanometer, to be afterwards described. It was in the form of these deflections, that the phenomena exhibited by a magnet, under the influence of a conducting wire, first presented themselves to Oersted in 1819.

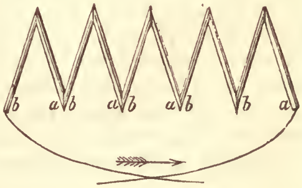
8. Thermo-electrical phenomena are produced from the effect of unequal tempera ture upon metals in contact. If heat be applied to the point *c* (fig. 83), at which two bars of bismuth and antimony *b* and *a* are soldered together, on connecting the free extremities by a wire, the whole is found to form a weak voltaic circle, with the induction from *b* through the wire to *a*. Hence in this thermo-polar arrangement the bismuth is the negative metal, and may be compared to the copper in the voltaic cell. If cold instead of heat be applied to *c*, a current also is established, but in an opposite direction to the former. Similar circuits may be formed of other metals, which may be arranged in the following order, the most powerful combination being formed of those metals which are most distant from each other in the following enumeration: bismuth, platinum, lead, tin, copper or silver, zinc, iron, antimony. When heated at their points of contact, the current proceeds through the wire from those which stand first to the last. According to Nobili, similar circuits may be formed with substances of which the conducting power is lower than that of the metals.

Fig. 83.



Several pairs of bismuth and antimony bars may be associated as in fig. 84, and the extreme bars being connected by a wire, form an arrangement resembling a compound voltaic circle. Upon heating the upper junctions, and keeping the lower ones cool, or on heating the lower ones and keeping the others cool, an induction is established in the wire, more intense than in the single pair of metals, but still very weak. The conducting wire strongly affects a needle, causing a deflection proportional to the inequality of temperature between the ends of the bars. Melloni's thermo-multiplier is a delicate instrument of this kind, which is even more sensitive to changes of temperature than the air-thermometer, and has afforded great assistance in exploring the phenomena of radiant heat (page 55).

Fig. 84.



In such a compound bar, also, unequal temperature may be produced, by making it the connecting wire of a single and weak voltaic circle; whereupon the metals become cold at their junction, if the induction is from the bismuth to the antimony, and hot at the same point if the induction is in the opposite direction. These are the converse of the preceding phenomena, in which electrical effects were produced by inequality of temperature.

9. The friction of different bodies is another source of electrical phenomena. One, at least, of the bodies rubbed together must not be a conductor, and in general two non-conductors are used. When a silk handkerchief or a piece of resin is rubbed upon glass, both are found, after separation, in a polar condition, and continue in it. The rubbing surface of the glass becomes and remains zincous, and that of the resin or silk is chlorous; and a molecular polarization is at the same time established through the whole mass of both the glass and resin, reaching to their opposite surfaces, which exhibit the other polarity. The powers thus appearing on the two rubbing surfaces, being manifestly different, were distinguished by the names of the bodies on which they are developed; that upon the glass as *vitreous* electricity (basylous affinity), and that upon the resin as *resinous* electricity (halogenous affinity).

In comparing the chemico-polarity excited by friction with that of the voltaic circle, we observe that the former is of high intensity but small in quantity, or affecting only a small number of trains of molecules. Also that the polar condition is more or less permanent, depending upon the insulation, and attended with a disturbance of the polar condition of surrounding bodies to a considerable distance, giving rise to electrical attractions and repulsions, or statical phenomena. If both the excited vitreous and resinous surfaces have a conducting metal, such as a sheet of tin-foil, applied to them, and each sheet have a wire proceeding from it, the wires and tin-foil are polarized similarly to the glass and the resin which they cover; and a saline body placed between the extremities of the wires, which are respectively a zincoid and chloroid, is polarized also, and decomposed. But the amount of decomposition, which is a true measure of the *quantity* of polar chains, is extremely minute compared with the amount of polarization in the voltaic circle. Thus, Mr. Faraday has calculated that the decomposition of one grain of water by zinc, in the active cell of the voltaic circle, produces as great an amount of polarization and decomposition in the cell of decomposition, as 950,000 charges of a large Leyden battery, of several square feet of coated surface; an enormous quantity of power, equal to a most destructive thunder-storm. The polarization from friction is therefore singularly intense, although remarkably deficient in quantity, or in the number of chains of polar molecules.

The kinds of matter susceptible of this intense polarization are so many and so various, such as glass, minerals, wood, resins, sulphur, oils, air, &c., as to make it difficult to suppose that the polar molecule is of the same chemical constitution in all of them, as it is in the electrolytes of the voltaic circle. Indeed, it must be admitted that all matter whatever may be forced into a polar condition by a most intense induction.

Electrical induction at a distance, Mr. Faraday has shown to be always an action of contiguous particles, chains of particles of air, or some other "dielectric," extending between the excited body which is inducing, and the induced body. His investigations of this subject led to the remarkable discovery that the intensity of electric induction at a constant distance from the inducing body is not always the same, but varies in different media, the induction through a certain thickness of shell-lac, for instance, being twice as great as through the same thickness of air. Numbers may be attached to different bodies which express their relative inductive capacities:—

Specific inductive	capacity of	air	1
"	"	glass	1.76
"	"	shell-lac	2
"	"	sulphur	2.24

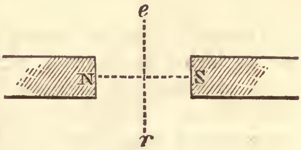
The inductive capacity of all gases is the same as that of air, and this property, it is remarkable, does not alter in these bodies with variations in their density.

10. Mr. Faraday has lately made the important discovery that a ray of polarized light passing through a transparent liquid or solid, is deflected, and takes a spiral direction, or has a motion of rotation communicated to it by the approximation of the pole of a powerful electro or natural magnet; the pole of the latter being so placed that the ray is in the direction of the lines of attraction of the magnet. The amount of the deflection of the ray varies in different transparent bodies, and is approximatively expressed for oil of turpentine by 11.8, heavy borate of lead glass 6.0, flint-glass 2.8, rock-salt 2.2, water 1, alcohol and ether less than water (Phil. Trans. 1846).

11. Operating with electro-magnets of the highest power, Mr. Faraday has obtained results of a fundamental nature respecting the magnetic capacity of different kinds of matter. The magnetic field being represented as in fig. 85, where N and S are the two poles, the dotted line N S connecting these poles, or line of magnetic force, is conveniently termed the axial direction, and the line *e r*, perpendicular to the former, the equatorial direction. When a bar of bismuth, two inches long, 0.33 inch wide, and 0.2 thick, was delicately suspended by a thread of

untwisted silk, and placed between the magnets, it arranged itself in the direction of *e r*, or equatorially. All kinds of solid, liquid, and even gaseous matter have a certain amount of tendency to place themselves, like the bismuth bar, across the axial or proper magnetic direction. This equatorial tendency is, however, overcome and negatived by the smallest proper magnetic property which bodies may possess, as this is the axial polarity, and causes the substance to set with its greatest length in the direction N S. Besides iron, nickel and cobalt, the usual magnetic metals, platinum, palladium and titanium, proved to be axial bodies. So are all the salts containing iron, nickel, or cobalt, as base. Even bottle glass is comparatively very magnetic, from the iron it contains; so is crown (window) glass, but not flint glass. The solutions of these salts are also magnetic. Crystals of the yellow ferrocyanide and red ferricyanide of potassium are not magnetic, but set equatorially. The iron, it will be remembered, belongs to the acid in these last salts. The salts of the oxides of the following metals proved magnetic, and Mr. Faraday is disposed to infer that the metals themselves are so — manganese, cerium, chromium. Paper and many other organic and mineral substances often contain enough of iron to make them fall into the same class.

Fig. 85.



The bodies which place themselves equatorially are named *diamagnetic*. The endless list of them is also headed by metals, which appear to possess this power in different degrees of intensity according to the following order: —

DIAMAGNETIC METALS.

Bismuth
Antimony
Zinc
Tin
Cadmium
Mercury
Silver
Copper

The other non-magnetic metals are diamagnetic in a less degree. This property is not sensibly impaired by heating the metals up to their fusing points. The property may be experimentally illustrated by pointed pieces of rock crystal, glass, phosphorus, sealing-wax, caoutchouc, wood, beef, bread, &c. (Phil. Trans. 1846).

Hot air and flame are more diamagnetic than cold or cooler air, so that a stream of the former spreads itself equatorially in ascending between magnetic poles. Of many gases and vapours tried by Mr. Faraday, oxygen was found to be the least diamagnetic; and this element appears to lower the equatorial tendency of the gases into which it enters as a constituent. Nitrogen is more highly diamagnetic than carbonic acid or hydrogen. In an atmosphere of carbonic acid gas (instead of air) between the magnetic poles, streams of hydrogen gas, coal gas, olefiant gas, muriatic acid, and ammonia, passed equatorially, and are therefore more diamagnetic. A stream of oxygen, which is so little diamagnetic, had, consequently, " the appearance of being strongly magnetic in coal gas, passing with great impetuosity to the magnetic axis, and clinging about it; and if much muriate of ammonia fume were purposely formed at the time, it was carried by the oxygen to the magnetic field with such force as to hide the ends of the magnetic poles. If, then, the magnetic action were suspended for a moment, this cloud descended by its gravity; but being quite below the poles, if the magnet were again rendered active, the oxygen cloud immediately started up and took its former place. The attraction of iron filings to a magnetic pole is not more striking than the appearance presented by the oxygen under these circumstances" (Faraday, Phil. Mag. xxxi. 415).

VOLTAIC INSTRUMENTS.

Daniell's constant battery. — A cell of this battery consists of a cylinder of copper 3½ inches in diameter, which experience has proved to the inventor to afford the most advantageous distance between the metallic surfaces, but which may vary in height from 6 to 20 inches, according to the power which it is wished to obtain. A membranous bag, formed of the gullet of an ox, is hung in the centre by a collar and circular copper plate, resting upon a rim within and near the top of the cylinder; and in this is suspended by a wooden cross-bar, a cylindrical rod of amalgamated zinc half an inch in diameter. Or a tube of porous earthenware, shut at the bottom, is substituted for the membrane with great convenience. The outer cell is charged with a mixture of 8 measures of water and 1 of oil of vitriol, which has been saturated with sulphate of copper, and portions of the solid salt are placed upon the circular copper plate, which is perforated like a colander, for the purpose of keeping the solution always in a state of saturation. The internal tube is filled with the same acid mixture without the salt of copper. A section of the upper part of one of these cells is here represented: *a b c d* (fig. 86) is the external copper cylinder; *e f g h*, the internal cylinder of earthenware, and *l m* the rod of amalgamated zinc. Upon a ledge *c d*, within an inch or two of the top of the cylinder, rests the cylindrical colander *i k*, which contains the copper salt, and both the sides and bottom of which are perforated with holes. A number of such cells may be connected into a compound circuit, with wires soldered to the copper cylinders, and fastened to the zinc by clamps and screws as shown below, in fig. 87 (Daniell's Int. to Ch. Phil.) Instead of the zinc cylinder a thick plate of laminated zinc is now generally used, which is more regularly amalgamated than the cast cylinder.

Fig. 86.

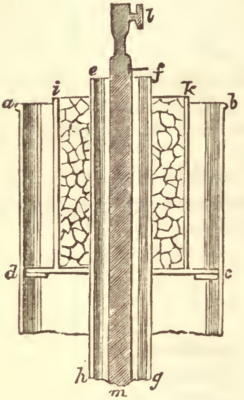
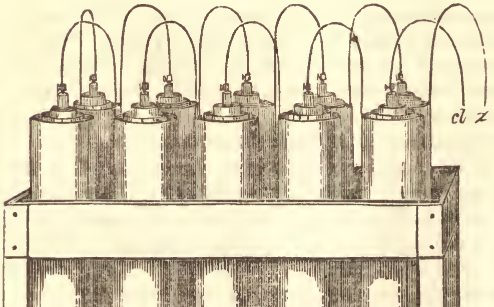


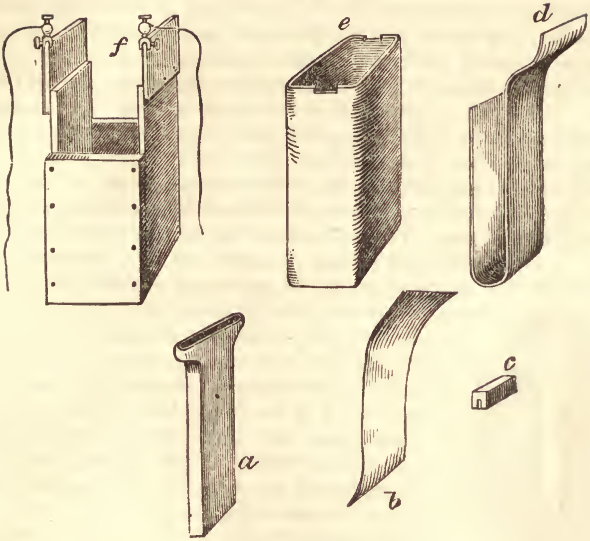
Fig. 87.



In this instrument the sulphate of zinc, formed by the solution of the zinc rod, is retained in the stoneware cylinder, and prevented from diffusing to the copper surface; while the hydrogen, instead of being evolved as gas on the surface of the latter metal, decomposes the oxide of copper of the salt there, and occasions a deposition of metallic copper on the copper plate. Such a circle will not vary in its action for hours together, which makes it invaluable in the investigation of voltaic laws. It owes its superiority principally to three circumstances: — to the amalgamation of the zinc, which prevents the waste of that metal by solution when the circuit is not completed; to the non-occurrence of the precipitation of zinc upon the copper surface; and to the complete absorption of the hydrogen at the copper surface, the adhesion of globules of gas to the metallic plates greatly diminishing, and introducing much irregularity into the action of a circle.

Grove's nitric acid battery. — In this battery the positive metal is amalgamated zinc, and the negative metal platinum, while the intermediate liquid is of two kinds, dilute sulphuric acid of sp. gr. 1.125 in contact with the zinc, and strong nitric acid

FIG. 88.



in contact with the platinum. In fig. 88, *a* represents a flat cell of porous earthenware, to contain the nitric acid and platinum plate; *b*, the platinum plate; *d*, the zinc plate, which is doubled up to include the porous cell; *e*, a cell of glazed earthenware to contain the sulphuric acid and zinc plate; *f*, a wooden frame to support the last cell, terminated above by copper plates provided with clamps, by which the terminal wires are attached. Two wooden wedges, such as *c*, are required to fix the upper end of the zinc plate on the one side, and the platinum plate on the other, as in fig. 89. Convenient dimensions for the principal parts are, the the external cell *e*, 4½ inches by 2¾ and 1¼; porous cell *a*, 4½ by 2½ and ⅜ inch; platinum plate 5 inches by 2½, and weighing about 10 grains in the square inch.

FIG. 89.

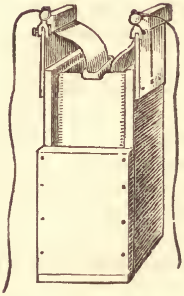
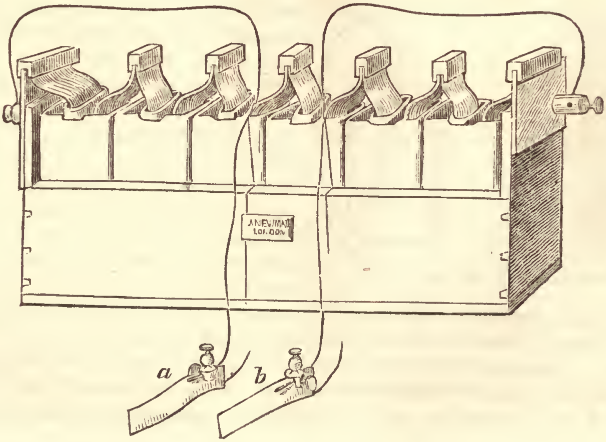


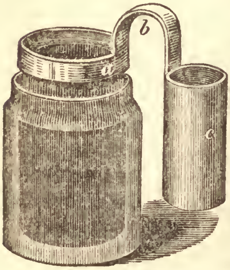
FIG. 90.



In fig. 90, six of these cells are placed together in a wooden frame, with the upper part of each end of the frame of stout sheet copper, to which the plates and wires can be clamped. The wires from the platinum and zinc ends of the battery, have platinum plates, *a* and *b*, attached to them as terminals. A battery of this size will evolve 8 or 10 cubic inches of mixed oxygen and hydrogen gases in the voltameter per minute. It is equal to several times as many cells of the preceding battery. The polarizing power is very intense, and little more decomposing power is gained by increasing the number of cells beyond five or six.

The carbo-zinc battery of Bunsen, which is much used on the continent, is a modification of the last construction, in which charcoal in contact with the nitric acid is substituted for platinum. The carbon is in the form of a hollow cylinder, and is made by coking pounded coal in a proper iron mould. By soaking the coke in sugar, and calcining a second time, great compactness is given to the cylinder. The latter is so large as to include the porous cell containing the zinc and acid, and is itself placed in a stout glass cylinder, of which the neck is contracted so as to support the coke cylinder (fig. 91). The zinc cylinder *c* is connected by a slip *b* and ring *a* of the same metal with the coke cylinder, of which the upper end is made a little conical to hold the ring. This battery has the advantage of enlarged negative surface, and provides ample space for the nitric acid.

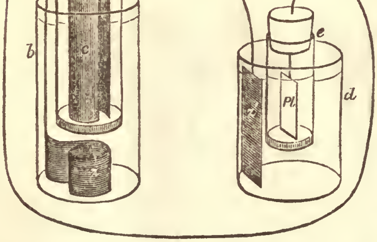
Fig. 91.



For other useful forms of the battery, such as that introduced by Mr. Smee, in which a thin sheet of silver covered by a deposit of platinum (platinized silver) is the negative metal, I must refer to works upon Electricity.

Bird's battery and decomposing cell. — To M. Becquerel we are particularly indebted for the investigation of the decomposing powers of feeble currents, sustained for a long time, the results of which are of great interest, both from the nature of the substances that can be thus decomposed, and from the form in which the elements of the body decomposed are presented, the slow formation of these bodies permitting their deposition in regular crystals (Traité Experimental de l'Electricité et du Magnétisme, par M. Becquerel). Dr. Golding Bird has also added to the number of bodies decomposed by such means, and contrived a simple form of the battery, which, with Becquerel's decomposing cell, renders such decompositions certain and easy (Phil. Trans. 1837, p. 37). The decomposing cell consists of a glass cylinder *a* (fig. 92) within another glass cylinder *b*. The inner cylinder *a* is 4 inches long, and 1½ inch in diameter, and is closed at the lower end by a plug of plaster of Paris 0.7 inch in thickness: this cylinder is fixed by means of wedges of cork within the other, which is a plain jar, about 8 inches deep by 2 inches in diameter. A piece of sheet copper *c*, 4 inches long and 3 inches wide, having a copper conducting wire soldered to it, is loosely coiled up and placed in the inner cylinder with the plaster bottom: a piece of sheet zinc *z*, of equal size, is also loosely coiled, and placed in the outer cylinder; this zinc likewise being furnished with a conducting wire. The outer cylinder is then nearly filled with a weak solution of common salt, and the inner with a saturated solution of sulphate of copper. The two fluids are prevented from mixing by the plaster diaphragm, and care being taken that they are at the same level in both the cylinders, the circle will afford, on joining the wires, a continuous current for weeks, the chloride of

Fig. 92.

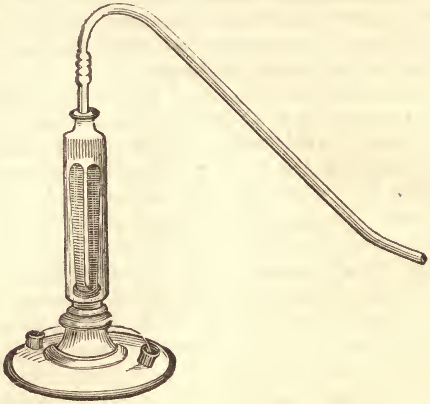


sodium and the sulphate of copper being very slowly decomposed. After it has been in action for some weeks, chloride of zinc is found in the outer cylinder: and beautiful crystals of metallic copper, frequently mixed with the ruby suboxide (closely resembling the native copper ruby ore in appearance), with large crystals of sulphate of soda, are found adhering to the copper plate in the smaller cylinder, especially on that part where it touches the plaster diaphragm.

The decomposing cell is the counterpart of the battery itself, consisting, like it, of two glass cylinders, one within the other, the smaller one *e* having a bottom of plaster of Paris fixed into it: this smaller tube may be about ½ inch wide and 3 inches in length, and is intended to hold the metallic or other solution to be decomposed, the external tube *d*, in which the other is immersed, being filled with a weak solution of common salt. In the latter solution a slip of amalgamated zinc-plate *z'*, soldered to the wire coming from the copper plate *c* of the battery, is immersed; and a slip of platinum foil *pl*, connected with the wire from the zinc plate *z* of the battery, is immersed in the liquor of the smaller tube, being held in its place by a cork, through which its wire passes. The whole arrangement is now obviously a pair of active cells, of which *c z'* is one metallic element, and *z pl* the other; and the fluid between *z* and *c* divided by the porous plaster diaphragm, one fluid element, and the fluid between *z* and *pl*, divided by a porous plaster diaphragm, another fluid element; although it will be convenient to speak of the last as the cell of decomposition. With a solution of chlorides or nitrates of iron, copper, tin, zinc, bismuth, antimony, lead or silver, in the smaller tube, Dr. Bird finds the metals to be reduced upon the surface of the platinum, generally but not invariably in possession of a perfect metallic lustre, always more or less crystalline, and often very beautifully so. The crystals of copper rival in hardness and malleability the finest specimens of native copper, and those of silver, which are needles, are white and very brilliant. The solution of fluoride of silicon in alcohol being introduced into the small tube by Dr. Bird, a deposition of silicon upon the platinum was found to take place in 24 hours, which was nearly black and granular, and is described as exhibiting a tendency to a crystalline form. From an aqueous solution of the same fluoride, a deposition of gelatinous silica was observed to take place around the reduced silicon, mixed with which, or precipitated in a zone on the sides of the tube, especially if of small diameter, frequently appear minute crystalline grains of silica or quartz, of sufficient hardness to scratch glass, and appearing translucent under the microscope. With a modification of the decomposing cell described, Dr. Bird succeeded in decomposing a solution of chloride of potassium, and obtained an amalgam of potassium. The inner tube *e* was replaced by a small glass funnel, the lower opening of which was stopped with stucco, and which thus closed retained a weak solution of the alkaline chloride poured into it. Every thing external to this funnel remaining as usual, mercury, contained in a short glass tube, like a thimble, was placed in the funnel, and covered by the liquid, and instead of the platinum plate, a platinum wire, coiled into a spiral at the extremity, was plunged into the mercury, the other end of this wire being connected with the zinc plate *z* of the battery. The circuit having been thus completed, the mercury had swollen in eight or ten hours to double its former bulk, and when afterwards thrown into distilled water, evolved hydrogen, and produced an alkaline solution. A solution of hydrochlorate of ammonia being substituted for that of chloride of potassium, in this experiment, the metal swells to five or six times its bulk in a few hours, and the semi-fluid amalgam of ammonium is formed. These feeble currents thus effect decompositions in the lapse of time, which batteries of the ordinary form, and considerable magnitude, may effect very imperfectly, or fail entirely in producing.

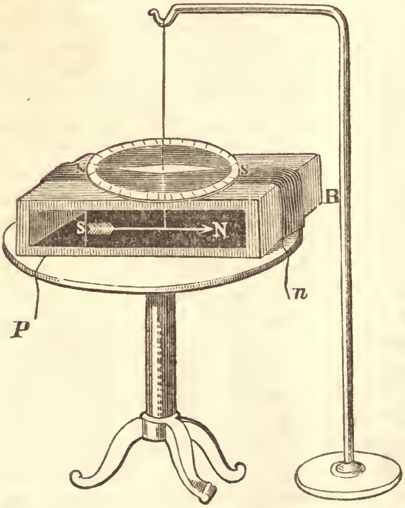
Volta-meter. — The decomposing power of a battery is represented by the quantity of oxygen and hydrogen gases evolved in a cell of decomposition containing dilute sulphuric acid. The volta-meter (figure 93) is simply a cell so charged, and of a proper form to allow of the gases evolved being collected and measured.

Fig. 93.



Galvanometer.—The sensibility of the magnetic needle to the influence of the conducting wire of a voltaic circle brought near it, has been applied to the construction of an instrument which will indicate the feeblest polarization or slightest current in the connecting wire. It consists of a pair of magnetic needles (fig. 94), fixed on one axis with their attracting poles opposite each other, so as to leave them little or no directive power, and render them astatic, which is delicately suspended by a single fibre of unspun silk. The lower needle is enclosed within a circle formed by a hank of covered wire B, of which *p* and *n* are the extremities. When the terminal wires of a battery are connected with the wires, the hank of wire of the galvanometer becomes part of the connecting wire, and the needle is deflected. The inductions proceeding in one direction above the needle and returning in the opposite direction below the needle, conspire to produce the same deflection; and the upper needle having its poles reversed, is deflected in the same direction, by the wire below it, as the lower needle is by the wire above that needle. Every turn of the wire also repeats the influence upon the needle, so that the deflection is increased in proportion to the number of turns or coils in the hank of wire. [*See Supplement,* p. 679.]

Fig. 94.



CHAPTER V.

NON-METALLIC ELEMENTS.

SECTION I.—OXYGEN.

Equivalent 8 (*hydrogen* = 1, *or* 100 *as the basis of the Oxygen Scale; density* 1105·6 (*air* = 1000); *combining measure* □ (*one volume*.)

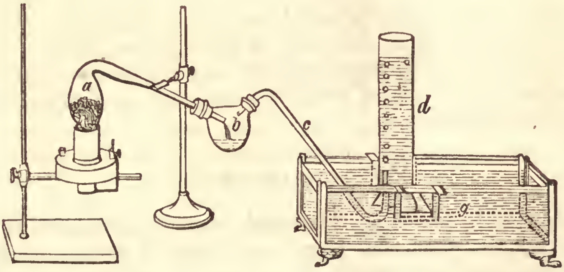
THE following thirteen of the sixty-two elementary bodies known,[1] are included in the class of non-metallic elements:—oxygen, hydrogen, nitrogen, carbon, boron, silicon or silicium, sulphur, selenium, phosphorus, chlorine, bromine, iodine, and fluorine. Of these, oxygen, from certain relations which it bears to all the others, and from its general importance, demands the earliest consideration.

The name oxygen is compounded of οξὺς, acid, and γενναω, I give rise to, and was given to this element by Lavoisier, with reference to its property of forming acids in uniting with other elementary bodies. Oxygen is a permanent gas, when uncombined, and forms one-fifth part of the air of the atmosphere.* In a state of combination, this element is the most extensively diffused body in nature, entering as a constituent into water, into nearly all the earths and rocks of which the crust of the globe is composed, and into all organic products, with a few exceptions. It was first recognised as a distinct substance by Dr. Priestley in England, in 1774, and about a year afterwards by Scheele in Sweden, without any knowledge of Priestley's experiments. From this discovery may be dated the origin of true chemical theory.

Preparation.—Oxygen gas is generally disengaged from some compound containing it, by the action of heat.

1. It was first procured by Priestley, by heating Red Precipitate (oxide of mercury), which is thereby resolved into fluid mercury and oxygen gas. To illustrate the formation of oxygen in this way, 200 grains of red precipitate may be introduced into the body of a small retort *a* of hard or difficultly fusible glass, and the retort united in an air-tight manner with a small globular flask *b*, having two openings, both closed by perforated corks, one of which admits the beak of the retort, and the

FIG. 95.



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[1] This number includes three elements — erbium, terbium, and ilmenium, of which the existence is doubtful.

* [*See Supplement*, p. 759.]

other an exit tube *c*, of glass, bent as in the figure. The extremity of the exit tube is introduced into a graduated jar capable of holding 50 or 60 cubic inches, and placed in an inverted position, full of water, upon the shelf of a pneumatic water-trough. Heat is then applied to the retort by means of an Argand spirit lamp powerful enough to raise it to a red heat, and maintain it at that temperature for a considerable time. The first effect of the heat is to expand the air in the retort, bubbles of which issue from the tube *c*, and rise to the top of the jar displacing water; but more gas follows, which is oxygen, and at the same time metallic mercury condenses in the neck of the retort and runs down into the intermediate flask *b*. When the red precipitate in the retort has entirely disappeared, the lamp may be extinguished, and the retort allowed to cool completely. The end of the exit tube *c* being now above the level of the water in the jar, which is nearly full of gas, a portion of the latter, equal in bulk to the air which first left the retort, will return to it, from the contraction of the gas within the retort. The jar will be found in the end to contain 44 cubic inches of gas, which is therefore the measure of oxygen produced in the experiment, and the flask to contain 185 grains of mercury. Now 44 cubic inches of oxygen weigh 15 grains; and a true analysis of the red precipitate has been effected, of which the result is, that 200 grains of that substance consist of—

185 grains mercury.
15 " oxygen, (44 cubic inches).
200

But oxygen gas is more generally derived from two other substances—oxide of manganese and chlorate of potassa.

2. When the gas is required in large quantity, and exact purity is immaterial, the oxide of manganese is preferred from its cheapness. This is a black, heavy mineral, found in Devonshire, in Hesse Darmstadt, and other localities, of which upwards of 40,000 tons are consumed annually in the manufactures of the country. It is called an oxide of manganese, because it is a compound of the metal manganese with oxygen. In explanation of what takes place when this substance is heated, it is necessary to state that manganese is capable of uniting with oxygen in several proportions, namely, one equivalent, or 27.67 parts of manganese, with 8, and with 16 parts of oxygen; and two equivalents of manganese with 24 parts of oxygen. These compounds are:—

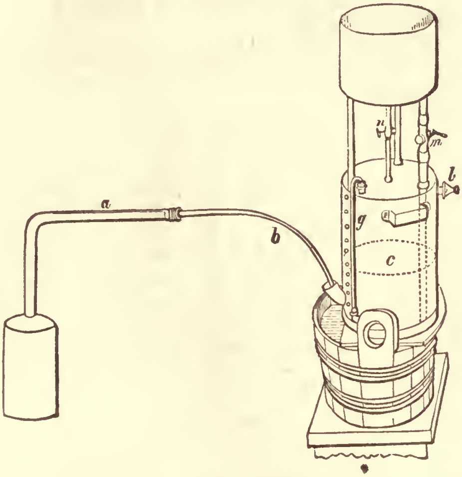
Protoxide of manganese	$Mn+O$.
Sesquioxide	$2Mn+3O$.
Binoxide, or native black oxide	$Mn+2O$.

Now the binoxide, however strongly heated, never loses more than one-third of its oxygen, being converted into a compound of the first two oxides: that is, three equivalents of binoxide (131.01 parts) lose two equivalents of oxygen (16 parts), and leave a compound of one eq. of sesquioxide and one eq. of protoxide; a change which may be thus expressed:—

$$3MnO_2 = \left\{\begin{array}{l} 2O \\ Mn^2O^3 + MnO. \end{array}\right.$$

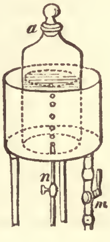
One of the malleable iron bottles in which mercury is imported is readily converted into a retort, in which the black oxide may be heated, by removing its screwed iron stopper, and replacing this by an iron pipe of three feet in length, one end of which has been cut to the screw of the bottle. This pipe may be bent like *a*, figure 96, if the bottle is to be heated in an open fire, or in a furnace open at the top. From 3 to 9 pounds of the oxide may be introduced as a charge, according to the quantity of gas to be prepared, each pound of good German manganese yielding about 1400 cubic inches, or 5.05 gallons of gas. Upon the first application of heat, water comes off, as steam, mixed occasionally with a gas which extinguishes flame; this is owing to the impurity of the oxide. The products may be allowed to escape, till the point of a wood-match, red without flame, applied to the orifice, is rekindled and made to burn with brilliancy; the gas is then sufficiently pure, and means must be taken for collecting it. A small flexible tin tube *b*, of any convenient length, is

Fig. 96.



adapted to the iron pipe, by means of a perforated cork, by which the gas is conveyed to a pneumatic trough, and collected in glass jars filled with water, as in the former experiment; or, as this process affords considerable quantities of oxygen, the gas is more generally conducted into the inferior cylinder or drum of a copper gas-holder *c*, full of water. The water does not flow out by the recurved tube whic forms the lower opening, but is retained in the vessel by the pressure of the atmosphere on the surface of the water in that tube, as water is retained in a bird's drinking-glass. But when the tin tube is introduced into the gas-holder by this opening, water escapes by it, in proportion as gas is thrown into the cylinder and rises in bubbles to the top. The progress of filling the gas-holder may be observed by the glass gauge-tube *g*, which is open at both ends, and connected with the top and bottom of the cylinder, so that the water stands at the same height in the tube as in the cylinder. Convenient dimensions for the cylinder itself are 16 inches in height by 12 in diameter; to fill which a charge of three pounds of manganese may be used. The gauge-tube is so apt to be broken, or to occasion leakage at its junctions with the cylinder, when the latter is large and unwieldy, that it is generally better to forego the advantage it offers, and dispense with this addition to the gas-holder. When applied to a small gas-holder, the ends of the tube are conveniently adapted to the openings of the cylinder, by means of perforated corks, which are afterwards covered by a mixture of white and red lead with a drying oil.

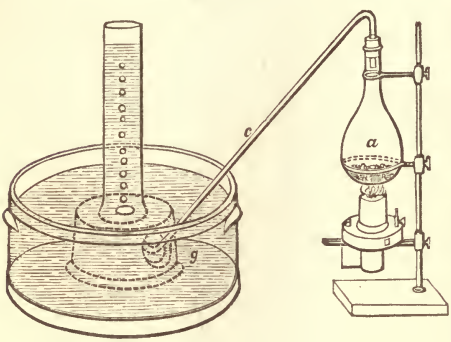
Fig. 97.



After the cylinder is filled, the lower opening by which the gas was admitted is closed by a good cork, or by a brass cap made to screw over it. The superior cylinder is an open water trough, connected with the inferior cylinder by two tubes provided with stop-cocks, *m* and *n*, one of which, *m*, is continued to the bottom of that vessel, and conveys water from the superior cylinder, while the other tube, *n*, terminates at the top of the inferior cylinder, and affords a passage by which the gas can escape from it, when water is allowed to descend by the other tube. The tube and perforation of the stopcock of *m* should be considerably wider than *n*. A jar *a* is filled with gas by inverting it full of water in the superior cylinder, over the opening of *n*, as exhibited in the figure, and allowing the gas to ascend from the inferior cylinder. Gas may likewise be obtained by the stopcock *l* (fig. 96), water being allowed to enter by *m* at the same time.

Oxygen may likewise be disengaged from oxide of manganese in a flask or retort, by means of sulphuric acid diluted with an equal bulk of water, but this is not a process to be recommended. When the quantity of oxygen required is not very large, it is better to have recourse to chlorate of potassa, which has also the advantage of giving a perfectly pure gas.

Fig. 98.



3. A well-cleansed Florence oil flask, the edges of the mouth of which have been heated and turned over so as to form a lip, with a bent glass tube and perforated cork fitted to it (fig. 98), forms a convenient retort in which about half an ounce of chlorate of potassa may be heated by means of a gas flame or Argand spirit lamp. The salt melts, although it contains no water, and when nearly red-hot emits abundance of oxygen gas. At one point of the decomposition, the effervescence may become so violent as to burst the flask, especially if the exit tube be narrow, unless the heat be moderated. The chlorate of potassa parts with all the oxygen it possesses, which amounts to 39·2 per cent. of its weight, and leaves a white hard salt, the chloride of potassium.

The only inconvenience attending the preceding process is the high temperature required, which would soften a retort or flask of flint glass. It was discovered, however, by M. Mitscherlich, that chlorate of potassa is decomposed at a much lower temperature when mixed with dry powders, upon which it exercises no chemical action, particularly metallic peroxides, such as the binoxide of manganese and the black oxide of copper. Nothing can answer better than the binoxide of manganese, after being made anhydrous by a short exposure to a red heat. Two parts of chlorate of potassa in powder, mixed with one part of the dried oxide, forms a useful "oxygen mixture," which may be made in quantity and preserved for occasional use.

From an atomic statement of the composition of chlorate of potassa, it appears that one equivalent of it (122·5 parts) contains six equivalents of oxygen (48 parts), namely five eq. in the chloric acid and one eq. in the potassa, the whole of which come off, leaving one equivalent of chloride of potassium (74·5 parts):—

$$KO + ClO_5 = \left\{ \begin{array}{l} 6O \\ KCl. \end{array} \right.$$

Half an ounce of chlorate of potassa should yield 270 cubic inches, or nearly a gallon of pure oxygen gas.

4. Another process for oxygen gas, proposed by Mr. Balmain, consists in heating in a retort 3 parts of the bichromate of potassa in powder, with 4 parts of undiluted sulphuric acid: the gas comes off in a continuous stream, and a mixture of sulphate of potassa and sulphate of sesquioxide of chromium remains behind in the retort. The decomposition which takes place is explained in the following formula:—

KO, Cr_2O_6 with $4\,SO_3$, give KO, SO_3 with $Cr_2O_3\;3SO_3$ and $3O$.

The bichromate of potassa loses one-half of the oxygen contained in the chromic acid, or about 16 per cent. of its weight; one ounce of salt yielding about 200 cubic inches of gas.

[5. When a perfectly pure gas is not required, oxygen may be obtained in large quantity from nitrate of potassa. The same apparatus is used as in the decomposition of black oxide of manganese: the nitre, of which 8 or 10 pounds may be used at once, is to be exposed to a well-regulated heat of a charcoal fire, the draught being urged or diminished in proportion to the rapidity of the flow of gas. A red heat is about the best temperature for the operation. The gas which comes over at this temperature contains about 96 per cent. of oxygen, and when after some time it is found necessary to urge the fire that the flow of gas may be kept up, the per centage diminishes, and may fall as low as 66. Two of the five equivalents of oxygen in the nitric acid are given off in the first part of the operation, and in the latter part the remaining oxygen with the nitrogen.—R. B.]

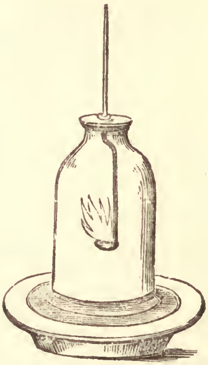
Properties.—Oxygen gas is colourless, and destitute of odour and taste. It is heavier than air in the ratio of 1105·6 to 1000, according to the latest careful determination, that of M. Regnault.[1]

At the temperature of 60°, and with the barometer at 30 inches, 100 cubic inches of oxygen gas weigh 34·19 grains (Regnault). One cubic inch, therefore, weighs 0·3419 gr., or about one-third of a grain. It has never been liquefied by cold or pressure.

Oxygen is so sparingly soluble in water, that when agitated in contact with that fluid no perceptible diminution of its volume takes place. But when water is previously deprived of air by boiling, and allowed to cool in a close vessel, 100 cubic inches of it dissolve $3\frac{1}{2}$ cubic inches of this gas.

If a lighted wax taper attached to a copper wire be blown out, and dipped into a vessel of oxygen gas, while the wick remains red-hot, it instantly rekindles with a slight explosion, and burns with great brilliancy. If soon withdrawn and blown out, it may be revived again in the same manner, and the experiment be repeated several times in the same gas. Lighted tinder burns with flame in oxygen, and red-hot charcoal with brilliant scintillations. Burning sulphur introduced into this gas in a little hemispherical cup of iron-plate with a wire attached to it, burns with an azure blue flame of considerable intensity. Phosphorus introduced into oxygen in the same manner, burns with a dazzling light of the greatest splendour, particularly after the phosphorus boils and rises through the gas in vapour. Indeed, all bodies which burn in air, burn with increased vivacity in oxygen gas. Even iron wire may be burned in this gas. For this purpose thin harpsichord wire should be coiled about a cylindrical rod into a spiral form. The rod being withdrawn, a piece of thread must be twisted about one end of the wire, and dipped into melted sulphur; the other end of the wire is to be fixed into a cork, so that the spiral may hang vertically. The sulphured end is then to be lighted, and the wire suspended in a jar of oxygen, open at the bottom, such as that represented in fig. 97, page 225, supported

Fig. 99.



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[1] Annales de Chimie, &c., 1845, 3e. ser. t. xiv. p. 211. The mean of three weighings previously made by MM. Dumas and Boussingault, was 1105·7 (ibid. t. viii. p. 201). Baron Wrede found 1105·2. At a much earlier period T. de Saussure obtained Regnault's number, 1105·6. These coincidences in the results of independent observers appear to prove that a close approximation has been made to the true density of this gas: an important datum. The earlier determination of MM. Dulong and Berzelius was 1102·6 (ibid. 1820, 2e. ser. t. xv. p. 386). According to M. Regnault, the weight of 1000 cubic centimeters (1 liter) of oxygen gas, at 32° F., barometer 29·92 inches (760 millimeters), is 1·4298 gramme. Hence, 1000 c. c. being equal to 61·028 English c. inches, and 1 gramme to 15·4440 English grains, 100 cubic inches of oxygen, at the specified temperature and pressure, weigh 36·1390 grains. Calculating with Regnault's coefficient for the expansion of air (page 40), 1 volume of oxygen will become 1·05701 volume, at 60°, and 100 cubic inches of oxygen will weigh 34·1898 grains at that temperature.

upon an earthenware plate. The wire is kindled by the sulphur, and burns with an intense white light, throwing out a number of sparks, or occasionally allowing a globule of fused oxide to fall; while the wire itself continues to fuse and burn till it is entirely consumed, or the oxygen is exhausted. The experiment forms one of the most beautiful and brilliant in chemistry. The globules of fused oxide are of so elevated a temperature, that they remain red-hot for some time under the surface of water, and fuse deeply into the substance of the stoneware plate upon which they fall.

[A portion of cast iron placed upon ignited charcoal and subjected to a stream of oxygen, soon melts and burns brilliantly, throwing off showers of bright sparks on all sides. — R. B.]

Oxygen gas is respirable, and indeed is constantly taken into the lungs from the atmosphere in ordinary respiration. When a portion of dark blood drawn from a vein is agitated with this gas, the colour becomes of a fine vermilion red. The same change occurs in the blood of living animals, during respiration, from the absorption of oxygen gas, which is required to maintain the animal heat. A small animal, also, such as a mouse or bird, lives four or five times longer in a vessel of oxygen than it will in an equal bulk of air. But the continued respiration of this gas in a state of purity is injurious to animal life. A rabbit is found to breathe it without inconvenience for some time, but after an interval of an hour or more the circulation and respiration are much quickened, and a state of great excitement of the general system supervenes; this is by and by followed by debility, and death occurs in from six to ten hours. The blood is found to be highly florid in the veins as well as the arteries, and, according to Broughton, the heart continues to act strongly after the breathing has ceased.

Oxygen may be made to unite with all the other elements except fluorine, and forms *oxides*, while the process of uniting with oxygen is termed *oxidation*. With the same element oxygen often unites in several proportions, forming a series of oxides, which are then distinguished from each other by the different prefixes enumerated under *Chemical nomenclature* (page 106). Many of its compounds are *acids*, particularly those which contain more than one equivalent of oxygen to one of the other element, and compounds of this nature are those which it most readily forms with the non-metallic elements: such as carbonic acid with carbon, sulphurous acid with sulphur, phosphoric acid with phosphorus. But oxygen unites in preference with single equivalents of a large proportion of the metallic class of elements, and forms bodies which are alkaline or have the character of *bases:* such as potassa, lime, magnesia, protoxide of iron, &c. A certain number of its compounds are neither acid nor alkaline, and are therefore called *neutral* bodies: such as the oxide of hydrogen or water, carbonic oxide, and nitrous oxide. The greater number of these neutral oxides are also protoxides.

It has already been stated that in a classification of the elements oxygen does not stand alone, but forms one of a small natural family along with sulphur, selenium, and tellurium. These elements also form acid, basic, and neutral classes of compounds, with the same bodies as oxygen does, of which the sulphur compounds are well known, and always exhibit a well-marked analogy to the corresponding oxides. Oxygen-acids unite with oxygen bases, and form neutral *salts:* so do sulphur-acids with sulphur-bases, selenium-acids with selenium-bases, and tellurium-acids with tellurium-bases.

The combinations of oxygen, like those of all other bodies, are attended with the evolution of heat. This result, which is often overlooked in other combinations, in which the proportions of the bodies uniting and the properties of their compound receive most attention, assumes an unusual degree of importance in the combinations of oxygen. The economical applications of the light and heat evolved in these combinations are of the highest consequence and value, and oxidation alone, of all chemical actions, is practised, not for the value of the products which it affords, and indeed without reference to them, but for the sake of the incidental phenomena attending it. Of the chemical combinations, too, which we habitually witness, those of oxygen are infinitely the most frequent, which arises from its constant presence and interference as a constituent of the atmosphere. Hence, when a body combines with oxygen, it is said to be *burned;* and instead of undergoing oxidation it is said to suffer *combustion;* and a body which can combine with oxygen and emit heat is termed a *combustible.* Oxygen, in which the body burns, is then said to support combustion, and called a *supporter* of combustion.

The heat evolved in combustion is definite, and can be measured. With this view it is employed to melt ice, to raise the temperature of water from 32° to 212°, or to convert water into steam, and its quantity is estimated by the extent to which it produces these effects. The heat from the oxidation of a combustible body is thus found to be as constant as any other of its properties. Despretz obtained, by such experiments, the results contained in the following table: —

HEAT FROM COMBUSTION.

1 pound of	pure charcoal	heats from 32° to 212°,	78	pounds of water.
—	charcoal from wood	—	75	—
—	baked wood	—	36	—
—	wood containing 20 per cent. of water	—	27	—
—	bituminous coal	—	60	—
—	turf	—	25 to 30	—
—	alcohol	—	67·5	—
—	olive oil, wax, &c	—	90 to 95	—
—	ether	—	80	—
—	hydrogen	—	236·4	—

The quantity of heat evolved appears to be connected with the proportion of oxygen consumed, for the greater the weight of oxygen with which a pound of any combustible unites, the more heat is produced. The following results indicate that the heat depends exclusively upon the oxygen consumed, four different combustibles in consuming a pound of oxygen affording nearly the same quantity of heat: —

HEAT OF COMBUSTION.

1 pound of oxygen	with hydrogen	heats from 32° to 212°,	29½	pounds of water.
—	with charcoal	—	29	—
—	with alcohol	—	28	—
—	with ether	—	28½	—

The quantity of combustible consumed in these experiments varied considerably, but the oxygen being the same, the heat evolved was nearly the same also. But when the same quantity of oxygen converted phosphorus into phosphoric acid, exactly twice as much heat was evolved, according to Despretz, as in the former experiments. The superior vivacity of the combustion of these and other bodies in pure oxygen, compared with air, depends entirely upon the rapidity of the process, and the larger quantity of combustible oxidated in a given time. A candle burns with more light and heat in oxygen than in air, but it consumes proportionally faster. [*See Supplement,* p. 751.]

Oxidation is often a very slow process, and imperceptible in its progress — as in the rusting of iron and tarnishing of lead exposed to the atmosphere. The heat being then evolved in a gradual manner is instantly dissipated, and never accumulates. But when the oxide formed is the same, the nature of the change effected is in no way altered by its slowness. Iron oxidates rapidly when introduced in a state of ignition into oxygen gas, and lead, in the form of the lead pyrophorus, which contains that metal in a high state of division, takes fire spontaneously and burns in the air; circumstances then favouring the rapid progress of oxidation.

Oxidation may also go on with a degree of rapidity sufficient to occasion a sensible evolution of heat, but without flame and open combustion. The absorption of oxygen by spirituous liquors in becoming acetic acid, and by many other organic substances, is always attended with the production of heat. The smouldering combustion of iron pyrites and some other metallic ores in the atmosphere, is a phenomenon of the same nature. Most bodies which burn with flame also admit of being oxidated at a temperature short of redness, and exhibit the phenomenon of *low combustion.* Thus, tallow thrown upon an iron plate not visibly red-hot, melts and undergoes oxidation, diffusing a pale lambent flame visible only in the dark (Dr. C. J. B. Williams). If the tallow be heated in a little cup with a wire attached, till it boils and catches fire, and the flame then be blown out, the hot tallow will still continue in a state of low combustion, of which the flame may not be visible, but which is sufficient to cause the renewal of the high combustion, if the cup is immediately introduced into a jar of oxygen gas. A candle newly blown out is sometimes rekindled in oxygen, although no point of the wick remains visibly red, owing to the continuance of this low combustion. When a coil of thin platinum wire, or a piece of platinum foil, is first heated to redness, and then held over a vessel containing ether or hot alcohol, the vapours of these substances, mixed with the air, oxidate upon the hot metallic surface, and may sustain the metal at a red heat for a long time, without the occurrence of combustion with flame. The product, however, of the low combustion of these bodies is peculiar, as is obvious from its pungent odour.

Combustion in air.—The affinity for oxygen of all ordinary combustibles is greatly promoted by heating them, and is indeed rarely developed at all except at a high temperature. Hence, to determine the commencement of combustion, it is commonly necessary that the combustible be heated to a certain point. But the degree of heat necessary to inflame the combustible is in general greatly inferior to what is evolved during the progress of the combustion, so that a combustible, once inflamed, maintains itself sufficiently hot to continue burning till it is entirely consumed. Here the difference may be observed between combustion and simple ignition. A brick heated till it be red-hot in a furnace, and taken out, exhibits ignition, but has no means within itself of sustaining a high temperature, and soon loses the heat which it had acquired in the fire, and on cooling is found unchanged.

The oxidable constituents of wood, coal, oils, tallow, wax, and all the ordinary combustibles, are the same, namely, carbon and hydrogen, which in combining with oxygen, at a high temperature, always produce carbonic acid and water; volatile bodies, which disappear, forming part of the aerial column that rises from the burning body. The constant removal of the product of oxidation, thus effected by its volatility, greatly favours the progress of combustion in such bodies, by permitting the free access of air to the unconsumed combustible. The influence of air in combustion is obvious from the facility with which a fire is checked or extinguished when the supply of air is lessened or withheld, and, on the contrary, revived and animated when the supply of air is increased by blowing up the fire. For the oxygen of the air being consumed in combining with the combustible, a constant renewal of it is necessary. Hence, if a lighted taper, floated by a cork upon water, be covered with a bell jar having an opening at top, such as that in which the iron-wire was burned, the taper will burn for a short time without change, then more and more feebly, in proportion as the oxygen is exhausted, and at last will expire. The air remaining in the jar is no longer suitable to support combustion, and a second lighted taper introduced into it by the opening at top is immediately extinguished.

In combustion, no loss whatever of ponderable matter occurs; nothing is annihilated. The matter formed may always be collected without difficulty, and is found to have exactly the weight of the oxygen and combustible together which have disappeared. The most simple illustrations of this fact are obtained in the combustion of those bodies which afford a solid product. Thus when two grains of phosphorus are kindled in a measured volume of oxygen gas, they are found converted after combustion into a quantity of white powder (phosphoric acid), which weighs 4½ grains, or the phosphorus acquires 2½ grains; at the same time 7½ cubic inches of oxygen disappear, which weigh exactly 2½ grains. In the same way, when iron-wire is burned in oxygen, the weight of solid oxide produced is found to be equal to that of the wire originally employed added to that of the oxygen gas which has disappeared. But the oxidation of mercury affords a more complete illustration of what occurs in combustion. Exposed to a moderate degree of heat for a considerable time in a vessel filled with oxygen, that metal is converted into red scales of oxide, possessing the additional weight of a certain volume of oxygen which has disappeared. But if the oxide of mercury so produced be then put into a small retort, and reconverted by a red heat into oxygen and fluid mercury, the quantity of oxygen emitted is found to be the same as had combined with the mercury in the first part of the operation; thus proving that oxygen is really present in the oxidized body.

The evolution of heat, which is the most striking phenomenon of combustion, still remains to be accounted for. It has been referred to the loss of latent heat by the combustible and oxygen, when, from the condition of gas or liquid, one or both become solid after combustion; to a reduction of capacity for heat, the specific heat of the product being supposed to be less than that of the bodies burned; and to a discharge of the electricities belonging to the different bodies, occurring in the act of combination. But the first two hypotheses are manifestly insufficient, and the last is purely speculative. The evolution of heat during intense chemical combination, such as oxidation, may be received at present as an ultimate fact; but if we choose to go beyond it, we must suppose that the heat exists in a combined and latent state in either the oxygen or combustible, or in both; that each of these bodies is a compound of its material basis with heat, the whole or a definite quantity of which they throw off on combining with each other. Heat, like other material substances, is here supposed not to evince its peculiar properties while in a state of combination with other matter, but only when isolated and free. This view gives a literal character to the expressions — liberation, disengagement, and evolution of heat during combustion. The phenomenon, it is to be remembered, is not confined to oxidation, but occurs in an equal degree in combinations without oxygen, and indeed to a greater or less extent in all chemical combinations whatever.

Fig. 100.

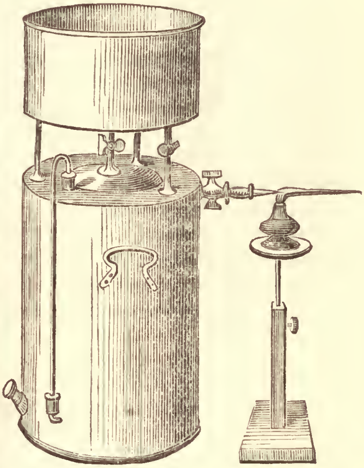
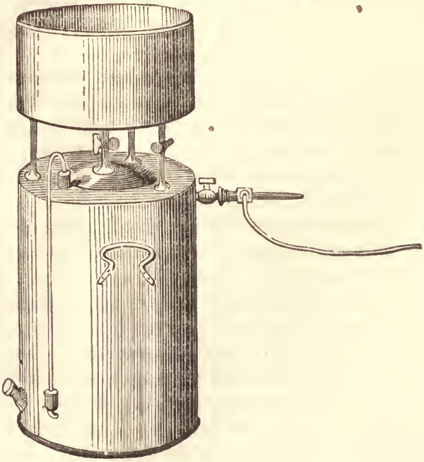


Fig. 101.



Pure oxygen has not as yet found any considerable application in the arts. But by the chemist it is applied to support combustion with the view of producing intense heat. A jet of this gas from a gas-holder (fig. 100), thrown upon the flame of a spirit-lamp, produces a blow-pipe flame of great intensity, adequate to fuse platinum. Or, if coal-gas be conducted to the oxygen jet (fig. 101), and the gases kindled as they issue together, a flame is produced of equally high temperature. Where a large quantity of oxygen is required, as in this application of it, the gas may be obtained by heating oxide of manganese in a cylinder of cast iron supported over a furnace, like the retort for coal gas. The calcined oxide does not regain its oxygen when afterwards exposed to the air, as was once supposed, but would still be of some value in the preparation of chlorine.

Ozone.—When electric sparks are taken through perfectly dry oxygen, a small portion of the gas acquires new properties, according to A. de la Rive, and is supposed by Berzelius to pass into an allatropic condition, in which it is named ozone from the peculiar odour it possesses, and which is somewhat metallic in character. The oxygen evolved from the decomposition of water in the voltameter (page 221) has the same odour. But the most ready mode of producing it is to place a few sticks of phosphorus in a quart bottle containing a little water at the bottom of it. While the sticks of phosphorus undergo the low combustion and are luminous, producing fumes of phosphorus acid and absorbing much oxygen, they give rise to the appearance of ozone in the air of the bottle in a manner not at present understood.

This substance has never been obtained in a separate state, but air impregnated with it acts very much as if a trace of chlorine gas were present, which ozone appears to resemble. In ozonized air, paper impregnated with a solution of iodide of potassium immediately becomes brown from the liberation of iodine; also paper containing a solution of sulphate of manganese soon becomes brown or black, from the formation of binoxide of manganese. The same air made to stream through a solution of the yellow-ferrocyanide of potassium converts it into the red ferricyanide. Ozone appears to be a gas not sensibly dissolved by water. It is destroyed by a heat of 140°, by contact with olefiant gas, and such other hydrocarbons as combine with chlorine, by phosphorus, or reduced silver. In the latter case nothing appears except oxide of silver. It passes, I find, through dry and porous stoneware, and is therefore not likely to be merely an electrical grouping of gaseous molecules. Professor Schönbein, who named this substance, and has made it the object of many investigations, considers it to be a volatile peroxide of hydrogen. [*See Supplement,* p. 759.]

SECTION II.

HYDROGEN.

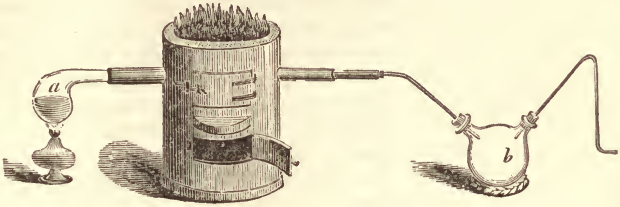
Equivalent 1, *as the basis of the Hydrogen Scale, or* 12·5 (*oxygen*=100); *symbol* H; *density* 69·26 (*air* 1000); *combining measure* ☐☐ (*two volumes*).

Hydrogen gas, which was long confounded with other inflammable airs, was first correctly described by Cavendish, in 1766. It does not exist uncombined in nature; at least the atmosphere does not contain any appreciable proportion of hydrogen. But it is one of the elements of water, and enters into nearly every organic substance. Its name is derived from ὑδωρ, water, and γενναω, I give rise to, and refers to its forming water when oxidated.

Preparation.—This element, although resembling oxygen in being a gas, appears to be more analogous to a metal in its relations to other elements. By heating oxide of mercury, it is resolved into oxygen and mercury; and several other metallic oxides, such as those of silver and gold, are susceptible of a similar decomposition. But some others are deprived of only a portion of their oxygen by the most intense heat, such as binoxide of manganese; and many, such as the protoxide of lead, are not decomposed at all by simple calcination. By igniting the latter oxide, however, mixed with charcoal, its oxygen goes off in combination with carbon, as carbonic oxide, and the lead is left. The oxide of hydrogen or water is similarly affected. Potassium and sodium brought into contact with it, at the temperature of the air, combine with its oxygen, and are converted into the oxides, potassa and soda; and hydrogen is consequently liberated.

Iron and many other metals decompose water, and become oxides, at a red heat. Hence, hydrogen gas is sometimes procured by transmitting steam through an iron tube filled with iron turnings, placed across a furnace and heated red-hot (fig. 102).

Fig. 102.



The vapour is obtained by boiling water in the small retort *a*, and the gas produced by its decomposition collected in the usual manner at the pneumatic trough. But it is necessary to have a flask *b* between the iron tube and the trough, to prevent an accident from the water of the trough finding access to the red-hot tube, in the event of condensation of the vapour in *a*.

Some other compounds of hydrogen are decomposed more easily than water, by iron and zinc. The chloride of hydrogen or hydrochloric acid is decomposed by these metals, and evolves hydrogen at the ordinary temperature of the air. But this gas is more generally obtained by putting pieces of zinc or iron into oil of vitriol or the concentrated sulphuric acid, diluted with six or eight times its bulk of water. The hydrogen is then derived from the decomposition of the proportion of water intimately united with the acid, as illustrated in the following diagram, zinc being used, and the quantities expressed:—

Before decomposition.				After decomposition.
49 oil of vitriol, or sulphate of water	Hydrogen	1	1	Hydrogen.
	Oxygen	8		
	Sulphuric acid	40		
32.52 zinc	Zinc	32.52	80.52	Sulphate of oxide of zinc.
81.52		81.52	81.52	

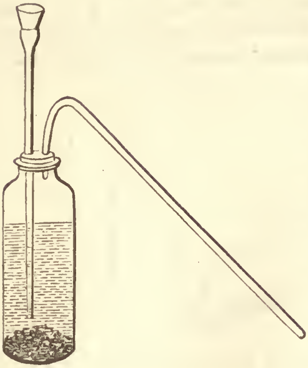
Or by symbols:—

$$HO+SO_3 \text{ and } Zn=ZnO+SO_3 \text{ and } H.$$

The zinc dissolves in the acid with effervescence, from the escape of hydrogen gas. It will be observed that the products after decomposition, mentioned in the last column, hydrogen and sulphate of oxide of zinc, are similar to those before decomposition, in the first column, zinc and sulphate of water; and that the change occurring is simply the *substitution* of zinc for hydrogen in the sulphate of water. The large quantity of water used with the acid is useful to dissolve the sulphate of zinc formed.

Zinc is generally preferred to iron, in the preparation of hydrogen, and is previously granulated, by being fused in a stone-ware crucible, and poured into water; if sheet zinc be used, which is better, it is cut into small pieces. The common glass retort may be used in the experiment, or a gas-bottle, such as the half-pound phial (see fig. 103), with a cork having two perforations fitted with glass tubes, one of which descends to the bottom of the bottle, and is terminated externally by a funnel for introducing the acid, whilst the other is the exit tube, by which the hydrogen

FIG. 103



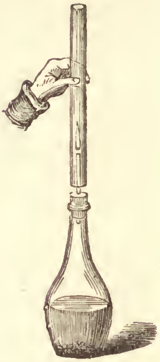
escapes. With an ounce or two of zinc in it, the bottle is two-thirds filled with water, and the undiluted acid added from time to time by the funnel, so as to sustain a continued effervescence. No gas escapes by the funnel tube, as its extremity within the bottle is always covered by the fluid. To produce large quantities, a half-gallon stone-ware jar may be mounted as a gas-bottle, with a flexible metallic pipe fitted to the cork as the exit tube. This gas may be collected, like oxygen, either in jars over the pneumatic trough, or in the gas-holder. The first jar or two filled will contain the air of the gas-bottle, and therefore must not be considered as pure hydrogen. One ounce of zinc is found to cause the evolution of 615 cubic inches of hydrogen gas.

Properties.—Hydrogen gas thus prepared is not absolutely pure, but contains traces of sulphuretted hydrogen and carbonic acid, which may be removed by agitating the gas with lime-water or caustic alkali. It has also a particular odour, which is not essential to hydrogen, as the gas evolved from the amalgam of sodium, acted on by pure water without acid, is perfectly inodorous. An oily compound of carbon and hydrogen, which appears to be the cause of this odour, may be separated in a sensible quantity from the gas prepared by iron, by transmitting it through alcohol. Of the pure gas, water does not dissolve more than 1½ per cent. of its bulk. Hydrogen has never been liquefied by cold or pressure.

Hydrogen is the lightest substance in nature, being sixteen times lighter than oxygen, and 14.4 times lighter than air; 100 cubic inches of it weigh only 2.14 grains. Soap-bubbles blown with this gas ascend in the atmosphere; and it is used, as is well known, to inflate balloons, which begin to rise when the weight of the stuff of which they are made and the hydrogen together, are less than the weight of an equal bulk of air. A light bag is prepared for making this experiment in the chamber, by distending the lining membrane of the crop of the turkey, which may weigh 35 or 36 grains, and when filled with hydrogen, about 5 grains more, or 41 grains; the same bulk of air, however, would weigh 50 or 51 grains; so that the little balloon when filled with hydrogen has a buoyant power of 9 or 10 grains. Larger bags are prepared for the same purpose, of gold-beaters' skin. Sounds produced in this gas were found by Leslie to be extremely feeble; much more feeble, indeed, than its rarity compared with air could account for. Hydrogen may be taken into the lungs without inconvenience, when mixed with a large quantity of air, being in no way deleterious; but it does not, like oxygen, support respiration, and therefore an animal placed in pure hydrogen soon dies of suffocation. A lighted taper is extinguished in the same gas.

Hydrogen is eminently combustible, and burns when kindled in the air with a yellow flame of little intensity, which moistens a dry glass jar held over it; the gas combining with the oxygen of the air in burning, and producing water. If before being kindled the gas is first mixed with enough of air to burn it completely, or with between two and three times its volume, and then kindled, the combustion of the whole hydrogen is instantaneous and attended with explosion. With pure oxygen, instead of air, the explosion is much more violent, particularly when the gases are mixed in the proportions of two volumes of hydrogen to one of oxygen, which are the proper quantities for combination. The combustion is not thus propagated through a mixture of these gases, when either of them is in great excess. The sound in such detonations is occasioned by the concussion which the atmosphere receives from the sudden dilatation of gaseous matter, in this case of steam, which is prodigiously expanded from the heat evolved in its formation.

FIG. 104.

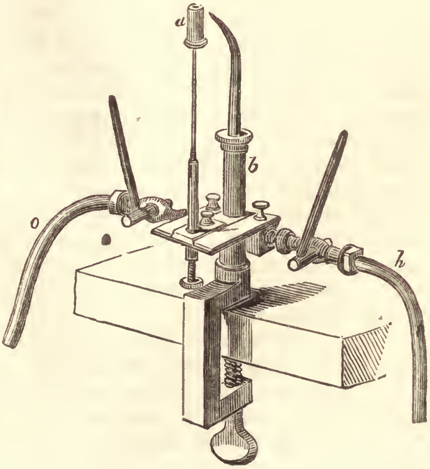


A musical note may be produced by means of these detonations, when they are made to succeed each other very rapidly. If hydrogen be generated in a gas-bottle (fig. 104), and kindled as it escapes from an upright glass jet having a small aperture, the gas will be found to burn tranquilly; but on holding an open glass tube of about two feet in length over the jet, like a chimney, the flame will be elongated and become flickering. A succession of little detonations is produced, from the gas being carried up and mixing with the air of the tube, which follow each other so quickly as to produce a continuous sound or musical note.

Several circumstances affect the combination of hydrogen with oxygen, which are important. These gases may be mixed together in a glass vessel, and preserved for any length of time without combining. But combination is instantly determined by flame, by passing the electric spark through the mixture, or even by introducing into it a glass rod, not more than just visibly red-hot. Hydrogen, indeed, is one of the more easily inflammable gases. If the mixed gases be heated in a vessel containing a quantity of pulverized glass, or any sharp powder, they begin to unite in contact with the foreign body in a gradual manner without explosion, at a temperature not exceeding 660°. The presence of metals disposes them to unite at a still lower temperature; and of the metals, those which have no disposition of themselves to oxidate, such as gold and platinum, occasion this slow combustion at the lowest temperature. In 1824, Dobereiner made the remarkable discovery that newly prepared spongy platinum has an action upon hydrogen mixed with oxygen, independently of its temperature, and quickly becomes red-hot when a jet of hydrogen is thrown upon it in air, combination of the gases being effected by their contact with the metal. In consequence of this ignition of the platinum the hydrogen itself is soon inflamed, as it issues from the jet. An instrument depending upon this action of platinum has been constructed for producing an instantaneous light. Afterwards, Mr. Faraday observed, that the divided state of the platinum, although favourable, is not essential to this action; and that a plate of that metal, if its surface be scrupulously clean, will cause a combination of the gases, accompanied with the same phenomena as the spongy platinum. This action of platinum is manifested at temperatures considerably below the freezing point of water, and in an explosive mixture largely diluted with air or hydrogen. Spongy platinum, made into pellets with a little pipe-clay, and dried, when introduced into mixtures of oxygen and hydrogen will be found to cause a gradual and silent combination of the gases, in whatever proportions they are mingled, which will not cease till one of them is completely exhausted. The theory of this effect of platinum is very obscure. It belongs to a class of actions depending upon surface, not confined to that metal, and by which other combustible vaporous bodies are affected besides hydrogen.

The flame of hydrogen, although so slightly luminous, is intensely hot; few combinations producing so high a temperature as the combustion of hydrogen. In the oxi-hydrogen blow-pipe, oxygen and hydrogen gases are brought by tubes *o* and *h* (fig. 105), from different gas-holders, and allowed to

FIG 105.



mix immediately before they escape by the same orifice, at which they are inflamed. This is most safely effected by fixing a jet for the oxygen within the jet of hydrogen (fig. 106), so that the oxygen is introduced into the middle of the flame of hydrogen —a construction first proposed by Mr. Maugham, [first made and used by Professor Hare.—R. B.] and adapted to the use of coal-gas instead of hydrogen by Mr. Daniell. (Phil. Mag. 3d ser., vol. ii. p. 57.) Each of the gases may be more conveniently contained in a separate air-tight bag of Macintosh cloth capable of holding from 4 to 6 cubic feet of gas, and provided with press-boards. These require to be loaded with two or three 56lbs., when in use, to send out the gas with sufficient pressure. At this flame the most refractory substances, such as pipe-clay, silica and platinum, are fused with facility, and the latter even dissipated in the state of vapour. The flame itself, owing to the absence of solid matter, is scarcely luminous, but any of the less fusible earths, upon which it is thrown, —a mass of quick-lime, for instance (*a*, fig. 105)—is heated most intensely, and diffuses a light, which, for whiteness and brilliancy, may be compared to that of the sun. With the requisite supply of the gases, this light may be sustained for hours, care being taken to move the mass of lime slowly before the flame, so that the same surface may not be long acted upon; for the high irradiating power of the lime is soon impaired, it is supposed from a slight agglutination of its particles occasioned by the heat. This light, placed in the focus of a parabolic reflector, was found to be visible, in the direction in which it was thrown, at a distance of 69 miles, in one experiment made by Mr. Drummond, when using it as a signal light. The heating effects are even more intense when the gases are forced into a common receptacle, and allowed to escape from under pressure, but there is the greatest risk of the flame passing back through the exit tube and exploding the mixed gases; an accident which would expose the operator to the greatest danger. Mr. Hemming's apparatus, however, may be used without the least apprehension. A common bladder is used to hold the mixture, and the gas before reaching the jet, at which it is burned, is made to pass through his safety tube. This consists of a brass cylinder about six inches long and three-fourths of an inch wide, filled with fine brass wire of the same length, which is tightly wedged by forcibly inserting a pointed rod of metal into the centre of the bundle. The conducting power of the metallic channels through which the gas has then to pass is so great as completely to intercept the passage of flame. A similar safety tube of smaller size is interposed at *b*, in fig. 105, of the first arrangement.

Fig. 106.

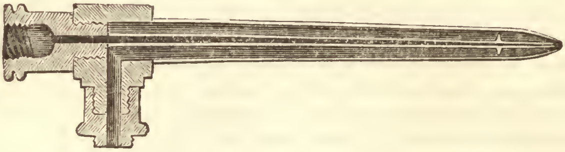
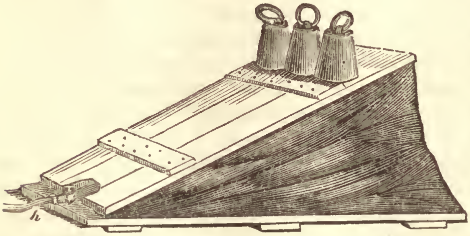


Fig. 107.



Hydrogen is capable of forming two compounds with oxygen, namely, water, which is the protoxide, and the binoxide of hydrogen.

The most important of the present applications of hydrogen gas is in the oxi-hydrogen blow-pipe. It has been superseded, as a material for inflating balloons, by coal gas, the balloon being proportionally enlarged to compensate for the less buoyancy of the latter gas. [*See Supplement*, p. 762.]

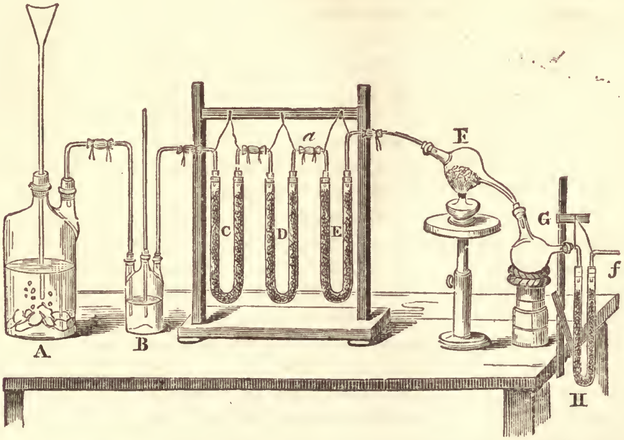
PROTOXIDE OF HYDROGEN.—WATER.

Equivalent 9, *or* 112.5 *on the oxygen scale; formula* H + O, *or* HO; *density* 1; *as steam* 622 (*air* 1000); *combining measure of steam* ☐☐.

Mr. Cavendish first demonstrated, in 1781, that the product of the combustion of hydrogen and oxygen is water. He burned known quantities of these gases in a dry glass vessel, and found that water was formed in quantity exactly equal to the weights of the gases which disappeared. It was afterwards established by Humboldt and Gay-Lussac, that the gases unite rigorously in the proportion of two volumes of hydrogen to one volume of oxygen, and that the water produced by their union occupies, while it remains in the state of vapour, exactly two volumes (page 126). The proportion of the constituents of water by weight was determined with great care by Berzelius and Dulong. Their method was to transmit dry hydrogen gas over a known weight of the black oxide of copper, contained in a glass tube, and heated to redness by a lamp. The gas was afterwards conveyed through another weighed tube containing the hygrometric salt, chloride of calcium. The hydrogen gas in passing over the oxide of copper, combines with its oxygen and forms water, which is carried forward by the excess of hydrogen gas, and absorbed in the chloride of calcium tube. The weight of this water being ascertained, the proportion of oxygen it contains is determined by ascertaining the loss which the oxide of copper has sustained: the difference is the hydrogen.

The apparatus for such an experiment is illustrated in the following diagram (fig. 108). The oxide of copper to be reduced is contained in F, a small flask of hard glass, having two openings, and heated by a spirit lamp. This flask communicates with another, G, intended to receive the greater part of the water produced in the experiment, which is followed by a bent tube H, containing fragments of pumice soaked in oil of vitriol, intended to receive the last portions. The hydrogen gas for this purpose must be very pure, and thoroughly dry. It is evolved slowly from a gas-bottle A, and passes through a second bottle B, and the bent tube C, both containing a concentrated solution of caustic potassa; and afterwards the bent tube D, containing a solution of chloride of mercury in pumice: and lastly through the bent tube F, containing oil of vitriol in pumice, proceeding thence entirely purified into F, and the excess of hydrogen gas escaping by *f*. Numerous most careful experi-

FIG. 108.



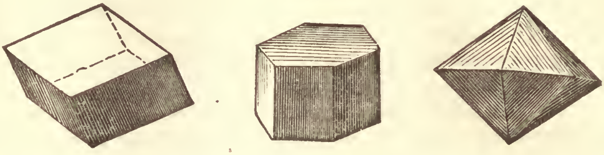
ments, lately executed in this manner by M. Dumas, prove that water consists exactly by weight of—

Oxygen	88·91	8
Hydrogen	11·09	1
	100·00	9

The oxygen and hydrogen are therefore combined exactly in the proportion of 8 to 1, as appears by the proportions of the last column. This experiment serves not only to determine rigorously the composition of water, but it offers also the best method of ascertaining the composition of such metallic oxides as are de-oxidized by hydrogen.

Properties. — When cooled down to 32°, water freezes, if in a state of agitation, but may retain the liquid condition at a lower temperature, if at rest (page 60); the ice, however, into which it is converted cannot be heated above 32° without melting. Ice is lighter than water, its specific gravity being 0·916; and one of the forms (fig. 109) of its crystal is a rhomboid, very nearly resembling Iceland spar.

Fig. 109.



Water is elastic and compressible, yielding, according to Oersted, 53 millionths of its bulk to the pressure of the atmosphere, and, like air, in proportion to the compressing force for different pressures. The peculiarities of its expansion by heat, while liquid, have already been fully described (page 38). Under a barometric pressure of 30 inches, it boils at 212°, but evaporates at all inferior temperatures. Its boiling point is elevated by the solution of salts in it, and the temperature of the steam from these solutions is not constantly 212°, as has been alleged, but that of the last strata of liquid through which the steam has passed. When mixed with air, the vapour of water has a tendency to condense, it is said, in vesicles, which inclose air; forming in this condition the masses of clouds, which remain suspended in the atmosphere from the lightness of the vesicles, the substance of mists and fogs, and "vapour" generally, in its popular meaning. The vesicles may be observed by a lens of an inch in focal length, over the dark surface of hot tea or coffee, mixed with an occasional solid drop which contrasts with them. According to the experiments of Saussure, made upon the mists of high mountains, these vesicles generally vary in size from the 1-4500th to the 1-2780th of an inch, but are occasionally observed as large as a pea. They are generally condensed by their collision into solid drops, and fall as rain; but their precipitation in that form is much retarded in some conditions of the atmosphere. It is proper to add, however, that Prof. J. Forbes and several other eminent meteorologists disbelieve entirely the existence of vesicular vapour.

It was lately discovered by Mr. Grove that the vapour of water is decomposed to a small but sensible extent by an exceedingly high temperature, and resolved into its constituent gases. If a small ball of platinum, of the size of a large pea, with a wire attached to it, be heated in the flame of the oxi-hydrogen blow-pipe to bright whiteness, and till it begins to show symptoms of fusion, and then plunged into hot water, minute bubbles of gas rise with the steam, which consist of a mixture of oxygen and hydrogen. Only a small portion of the steam, not amounting to even one-thousandth part of the whole produced (it is supposed) suffers decomposition. The occurrence of a decomposition in such circumstances, which is unquestionable, appears singular, seeing that oxygen and hydrogen certainly combine at the same, or even a higher, temperature in the flame of the blow-pipe, which is employed to heat the platinum ball. The combustion in the blow-pipe may, indeed, be incomplete, but this is unlikely, for I find that when the mixed gases are exploded in a glass tube, the combustion is so complete that certainly not one part in four thousand, if any portion whatever, escapes combustion. It is a question whether the decomposition of the steam by ignited platinum is not an exhibition of the deoxidizing action of light rather than the effect of heat; the blow-pipe flame itself being scarcely visible, while the decomposing platinum, although necessarily of a lower temperature, is highly incandescent.

A cubic inch of water at 62°, Bar. 30 inches, weighs in air 252.458 grains. The imperial gallon has been defined to contain 10 pounds avoirdupois (70,000 grains) of distilled water at that temperature and pressure. Its capacity is therefore 277.19 cubic inches. The specific gravity of water at 60° is 1, being the unit to which the densities of all other liquids and solids are conveniently referred; it is 815 times heavier than air at that temperature.

In its chemical relations water is eminently a neutral body. Its range of affinity is exceedingly extensive, water forming definite compounds, to all of which the name *hydrate* is applied, with both acids and alkalies, with a large proportion of the salts, and indeed with most bodies containing oxygen. It is also the most general of all solvents. Gay-Lussac has observed that the solution of a salt is uniformly attended with the production of cold, whether the salt be anhydrous or hydrated, and that, on the contrary, the formation of a definite hydrate is always attended with heat; a circumstance which indicates an essential difference between solution and chemical combination (Ann. de Ch. et de Phys. t. lxx. p. 407). Even the dilution of strong solutions of some salts, such as those of ammonia, occasions a fall of temperature. The solvent power of water for most bodies increases with its temperature. Thus at 57° water dissolves one-fourth of its weight of nitre, at 92° one-half, at 131° an equal weight, and at 212° twice its weight of that salt. Solutions of such salts, saturated at a high temperature, deposit crystals on cooling. But the crystallization of some saturated solutions is often suspended for a time, in a remarkable manner, and afterwards determined by slight causes. Thus, if two pounds of crystallized sulphate of soda be dissolved in one pound of water, with the assistance of heat, and the solution be filtered while hot through paper, to remove foreign solid particles, and then set aside in a glass matrass, with a few drops of oil on its surface, it may become perfectly cold without crystallization occurring. Violent agitation even may not cause it to crystallize. But when any solid body, such as the point of a glass rod, or a grain of salt, is introduced into the solution, crystals immediately begin to form about the solid nucleus, and shoot out in all directions through the liquid. The solubility of many salts of soda and lime does not increase with the temperature, like that of other salts.

Water is also capable of dissolving a certain quantity of air and other gases, which may again be expelled from it by boiling the water, or by placing it in vacuo. Rain-water generally affords 2½ per cent. of its bulk of air, in which the proportion of oxygen gas is so high as 32 per cent., and in water from freshly melted snow 34.8 per cent., according to the observations of Gay-Lussac and Humboldt, while the oxygen in atmospheric air does not exceed 21 per cent. Boussingault finds that the quantity of air retained by water, at an altitude of 6 or 8000 feet, is reduced to one-third of its usual proportion. Hence it is that fishes cannot live in Alpine lakes, the air contained in the water not being in adequate quantity for their respiration The following table exhibits the absorbability of different gases by water deprived of all its air by ebullition: —

100 cubic inches of water at 60° and 30 Bar., absorb of

	Dalton.	Henry.	Saussure.
Hydrosulphuric acid	100 C. I.	106	253
Carbonic acid	100	100	106
Nitrous oxide	100	77.6	76
Olefiant gas	12.5	14	15.5
Oxygen	3.7	3.55	6 5
Carbonic oxide	1.56	2.01	6.2
Nitrogen	1.56	1.47	4.2
Hydrogen	1.64	1.53	4.6

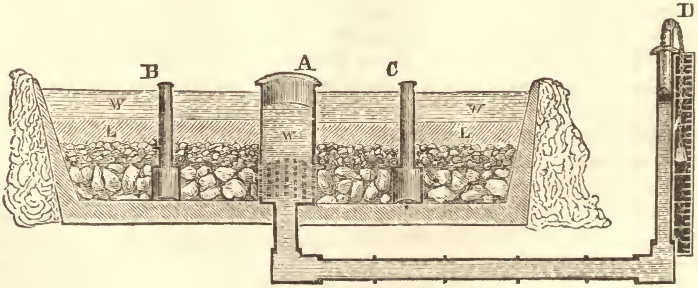
The results of Saussure are probably nearest the truth for hydrosulphuric acid and nitrous oxide, but for the other gases those of Dalton (Manchester Memoirs, 2d ser. p. 287) and Henry (Phil. Trans. 1843, pp. 29, 274) are most to be depended on.*

Uses. — Rain received after it has continued to fall for some time may be taken as pure water, excepting for the air it contains. But after once touching the soil, it becomes impregnated with various earthy and organic matters, from which it can only be completely purified by distillation. A copper still should be used for that purpose, provided with a copper or block-tin worm, which is not used for the distillation of spirits, as traces of alcohol remaining in the worm and becoming acetic acid, cause the formation of acetate of copper, which would be washed out and contaminate the distilled water. The use of white lead cement about the joinings of the worm is also to be avoided, as the oxide of lead is readily dissolved by distilled water. The first portions of the distilled water should be rejected, as they often contain ammonia, and the distillation should not be carried to dryness.

Water employed for economical purposes is generally submitted to a more simple process, that of filtration, by which it is rendered clear and transparent by the removal of matter mechanically suspended in it. Such foreign matter may often be removed in a considerable degree by subsidence, on which account it is desirable that the water should stand at rest for a time, before being filtered. The filtration of liquids generally is effected, on the small scale, by allowing them to flow through unsized or filter paper, and that of water, on the large scale, by passing it through beds of sand. The sand preferred for that purpose is not fine, but gravelly, and crushed cinders or furnace clinkers may be substituted for it. Its function, as that also of the paper in the chemist's filter, is to act as a *support* for the finer particles of mud or precipitate which are first deposited on its surface, and form the bed that really filters the water. When the mud accumulates so as to impede the action of the sand filter, the surface of the sand is scraped, and an inch or two of it removed.

Fig. 110 is a section of the water-filter, as it is usually constructed for public

Fig. 110.



* [*See Supplement*, p. 763.]

works in Lancashire. An excavation of about six feet in depth, and of sufficient extent, is lined to a considerable thickness with well puddled clay, to make it watertight. Upon the clay floor is laid first a stratum of large stones, then a stratum of smaller stones, and, finally, a bed of coarse sand or gravel, L L. To allow the air to escape from the lower beds, small upright tubes, open at both ends, B and C, are inserted in these beds, and rising above the surface of the water W W. The filtered water enters, from the lowest bed, into a large open iron cylinder A, the lower part of which is perforated for that purpose. The filtered water stands at the same height in the gauge tube D as in A; this height is observed by means of a float balanced by a weight which traverses a scale of feet and inches at D.

Upward filtration through a bed of sand is sometimes practised, but it has the disadvantage that the filter cannot be cleaned in the manner indicated. Filtering under high pressure, and with great rapidity, has been practised in a very compact apparatus, consisting of a box, not above three feet square, filled with sand. This filter, which becomes speedily choked with the mud it detains, is cleansed by suddenly reversing the direction in which the water is passing through the box, which occasions a shock that has the effect of loosening the sand, and allowing the water to bring away the mud. The action of such a filter, erected at the Hôtel-Dieu of Paris, was favourably reported on by M. Arago (Annal. de Chim. et de Phys. t. lxv. p. 428).

Matter actually dissolved in water is not affected by filtration. No repetition of the process would withdraw the salt from sea-water and make it fresh. Hence the impregnation of peaty matter, which river water generally contains, and to the greatest extent in summer, when the water is concentrated by evaporation, is not removed by filtering. Animal charcoal is the proper substance for discolouring liquids, as it withdraws organic colouring matter, even when in a state of solution.

In the process of clarifying liquors by dissolving in them the white of egg and other albuminous fluids, the temperature is raised so as to coagulate the albumen, which thus forms a delicate net-work throughout the liquid, and is afterwards thrown up as scum in the boiling, carrying all the foreign matter suspended in the liquid along with it.

Gelatine, isinglass, or other "finings," added to wine in a turbid state, produce a precipitate with its tannin, which carries down all suspended matter; and on the settling of this precipitate, or its separation by filtering, the wine is found transparent.

The most usual earthy impurities in water, occasioning its hardness, are sulphate of lime, and the carbonate of lime dissolved in carbonic acid, both of which are precipitated on boiling the water, and occasion an earthy incrustation of the boiler.

So far as this precipitation is due to carbonate of lime it may be avoided by adding hydrochlorate of ammonia to the water, by which the lime is converted into chloride of calcium and becomes soluble. Water containing carbonate of lime may be also softened by the addition of lime-water, as recommended by Professor Clark. Thames water requires for this purpose the addition of about one-fourteenth of its bulk of lime-water. This action of lime-water will be explained under carbonic acid.

When waters contain iron, they are termed *chalybeate:* this metal is most frequently in the state of carbonate dissolved in carbonic acid, and rarely in a proportion exceeding one grain in a pound of water. The *sulphurous* waters, which are recognised by their peculiar odour, and by blackening silver and salts of lead, contain hydrosulphuric acid in a proportion not exceeding the usual proportion of air in spring water, and generally no oxygen. *Saline* waters for the most part contain various salts of lime and magnesia, and generally common salt. Their density is always considerably higher than that of pure water. *Sea-water* contains 3½ per cent. of saline matter, and has a density 1.0274. Its composition is interesting, as the sea comes to be the grand depository of all the soluble matter of the globe. A minute analysis of the water of the English Channel, executed by Mr. Schweitzer, is subjoined:—

Sea-water of the English Channel.	Grains.
Water	964.74372
Chloride of sodium	27.05948
Chloride of potassium	0.76552
Chloride of magnesium	3.66658
Bromide of magnesium	0.02929
Sulphate of magnesia	2.29578
Sulphate of lime	1.40662
Carbonate of lime	0.03301
	1000.0000

In addition to those constituents, distinct traces of iodine and of ammonia were detected (Phil. Mag. 3d ser. vol. xv. p. 58). According to Professor Forchammer, the whole quantity of saline matter in water from different parts of the Atlantic varied from 35.7 parts (German sea) to 36.6 parts (tropics) in 1000 parts of the water. The relative proportion of the salts in the water of different seas varied very little (Reports of the British Association, 1846, p. 90).

BINOXIDE OF HYDROGEN.

Equivalent, 17, *or* 212.5 *on Oxygen Scale; formula* $H+2O$ *or* HO_2.

The second compound of hydrogen and oxygen is a liquid, containing twice as much oxygen as water, and is a body possessed of very extraordinary properties. It was discovered by Thenard, in 1818, who prepared it by a long and intricate process.

Preparation.—The formation of the binoxide of hydrogen depends upon the existence of a corresponding binoxide of barium. The latter is obtained by calcining pure nitrate of baryta at a high temperature in a porcelain retort, and afterwards exposing the earth baryta or protoxide of barium, which is left, in a porcelain tube heated to redness, to a stream of oxygen gas, which the protoxide rapidly absorbs, becoming binoxide. Treated with a little water, the binoxide of barium slakes and falls to powder, forming a hydrate, of which the formula is BaO_2+HO. Dilute acids have a peculiar action upon this hydrate, which will be easily understood, if the binoxide of barium is represented as the protoxide united with an additional equivalent of oxygen, or as $BaO+O$. They combine with the protoxide of barium, forming salts of baryta, and the second equivalent of oxygen, instead of being liberated in consequence, unites with the water of the hydrate, the HO of the preceding formula giving rise to $HO+O$ or the binoxide of hydrogen, which dissolves in the water. Although it would be inconvenient to abandon the systematic name binoxide of hydrogen for this compound, still it must be allowed that the properties of the body, as well as its mode of preparation, are more favourable to the idea of its being a combination of water with oxygen, or *oxygenated water,* as it was first named by its discoverer, than a direct combination of its elements. It is recommended by Thenard to dissolve the binoxide of barium in hydrochloric acid considerably diluted with water, and to remove the baryta by sulphuric acid, which forms an insoluble sulphate of baryta. The hydrochloric acid, again free in the liquor, is saturated a second time with binoxide of barium, and precipitated; and after several repetitions of these two operations, the hydrochloric acid itself is removed by the cautious addition of sulphate of silver, and the sulphuric acid of the last salt by solid baryta. Such is an outline of the process, but its success requires attention to a number of minute precautions, which are fully detailed in the Traité de Chemie of the author quoted (vol. i. p. 479, 6th ed.) The weak solution of binoxide of hydrogen, which this process affords, may be concentrated by placing it with a vessel of strong sulphuric acid under the receiver of an air-pump, until the solution attains a density of 1.452, when the binoxide itself begins to rise in vapour without change. It then contains 475 times its volume of oxygen.

M. Pelouze abridges this process considerably by employing hydro-fluoric acid or fluosilicic acid, in place of hydrochloric acid, to decompose the binoxide of barium. By this operation, the baryta separates at once with the acid, in the state of the insoluble fluoride of barium, and nothing remains in solution but the binoxide of hydrogen. After thus decomposing several portions of binoxide of barium successively in the same liquor, the fluoride of barium may be separated by filtration, and the binoxide of hydrogen, which is still dilute, be concentrated by means of the air-pump.

Properties.—Binoxide of hydrogen is a colourless liquid resembling water, but less volatile, having a metallic taste, and instantly bleaching litmus and other organic colouring matters. It is decomposed with extreme facility, effervescing from escape of oxygen at a temperature of 59°, and when suddenly exposed to a greater heat, such as 212°, actually exploding from the rapid evolution of that gas. It is rendered more permanent by dilution with water, and still more so by the addition of the stronger acids, while alkalies have the opposite effect.

The circumstances attending the decomposition of this body are the most curious facts in its history. Many pure metals and metallic oxides occasion its instantaneous resolution into water and oxygen gas, by simple contact, without undergoing any change themselves, affording a striking illustration of catalysis (page 186); and this decomposition may excite an intense temperature, the glass tube in which the experiment is made sometimes becoming red hot. Some protoxides absorb at the same time a portion of the oxygen evolved, and are raised to a higher degree of oxidation, but most of them do not; and certain oxides, such as the oxides of silver and gold, are reduced to the metallic state, their own oxygen going off along with that of the binoxide of hydrogen. The decomposition of these metallic oxides cannot be ascribed to the heat evolved, for oxide of silver is reduced in a very dilute solution of the binoxide of hydrogen, although the decomposition is not then attended with a sensible elevation of temperature. The metallic oxides which are decomposed in this remarkable manner are originally formed by the decomposition of other compounds, and not by the direct union of their elements, which, in fact, exhibit little affinity for each other. In this general character they agree with binoxide of hydrogen itself.

Uses.—The binoxide of hydrogen is a substance which it is exceedingly desirable to possess, with the view of employing it in bleaching, and for other purposes, as a powerful oxidating agent. But the expense and uncertainty of the process for preparing this compound have hitherto prevented any application of it in the arts, or even its occasional use as a chemical re-agent.

SECTION III.

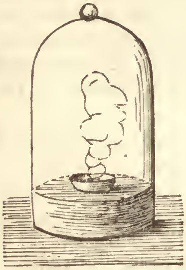
NITROGEN.

Synonyme, AZOTE. *Equiv.* 14, *or* 175 (O=100); *symbol* N; *density* 971.37; *combining measure* ☐☐.

Dr. Rutherford, of Edinburgh, examined the air which remains after the respiration of an animal, and found that after being washed with lime-water, which removes carbonic acid, it was incapable of supporting either combustion or respiration. He concluded that it was a peculiar gas. Lavoisier afterwards discovered that this gas exists in the air of the atmosphere, forming indeed 4-5ths of that mixture, and gave it the name azote, (from α, privative, and ζωη, life), from its inability to support respiration. It was afterwards named nitrogen by Chaptal, because it is an element of nitric acid. Besides existing in air, nitrogen forms a constituent of most animal and of many vegetable substances. In a natural arrangement of the elements, nitrogen appears to have its place between oxygen and phosphorus (page 147).

*Preparation.**—Nitrogen is generally procured by allowing a combustible body to combine with the oxygen of a certain quantity of air confined in a vessel. For that purpose a little metallic or porcelain cup may be floated, by means of a cork, on the surface of the water-trough. A few drops of alcohol are then introduced into the cup, or a small piece of phosphorus is placed in it, and being kindled, a tall bell jar is held over the cup, with its lip in the water. The combustion soon terminates, and the water of the trough rises in the jar. Alcohol does not consume the oxygen entirely, a small portion of it still remaining mingled with the nitrogen; a certain quantity of carbonic acid gas is also produced by its combustion. But the combustion of phosphorus exhausts the oxygen completely, and leaves nitrogen unmixed with any other gas.

Fig. 111.



Nitrogen may be likewise conveniently obtained by conducting chlorine gas into diluted ammonia. For delicate purposes of research this gas is best prepared by carrying air through a tube filled with reduced metallic copper in a pulverulent form, and heated to redness, by which the oxygen is entirely absorbed.

Properties.—Nitrogen gas is tasteless and inodorous; has never been liquefied, and is less soluble in water than oxygen. It is a little lighter than air, (specific gravity .9714), which possesses the mean density of 79.1 volumes of nitrogen and 20.9 volumes of oxygen. Nitrogen is a singularly inert substance, and does not unite directly with any other single element, so far as I am aware, under the influence of light or of a high temperature, unless, perhaps, oxygen and carbon. A burning taper is instantly extinguished in this gas, and an animal soon dies in it, not because the gas is injurious, but from the privation of oxygen, which is required in the respiration of animals. Nitrogen appears to be chiefly useful in the atmosphere, as a diluent of the oxygen, thereby repressing to a certain degree the activity of combustion and other oxidating processes. Of the fixation of free nitrogen of plants, there is no evidence. When heated with oxygen, nitrogen does not burn like hydrogen, nor undergo oxidation. But nitrogen may be made to unite with oxygen by transmitting several hundred electric sparks through a mixture of these gases in a tube, with water or an alkali present, and nitric acid is produced. The water formed by the combustion of hydrogen in air, or of a mixture of hydrogen and nitrogen in oxygen, has often an acid reaction, which is due to a trace of nitric acid. But when the hydrogen is mixed with air in excess, so as to prevent great elevation of temperature during the combustion, the oxidation of the nitrogen does not take place (Kolbe). Nitric acid is also a product of the oxidation of a variety of compounds containing nitrogen. Ammonia mixed with air, on passing over spongy platinum at a temperature of about 572°, is decomposed, and the nitrogen it contains is completely converted into nitric acid, by combining with the oxygen of the air. Cyanogen and air, under similar circumstances, occasion the formation of nitric and carbonic acids. (Kuhlman, Phil. Mag. 3d ser., vol. xiv. p. 157). Nitric acid is also largely produced by the oxidation of organic matters during putrefaction in air, when an alkali or lime is present, as in the natural nitre soils and artificial nitre beds.

A suspicion has always existed that nitrogen may be a compound body, but it has resisted all attempts to decompose it, and the evidence of its elementary character is equally good with that of most other bodies reputed simple. Before considering the compounds of nitrogen with oxygen, we may notice the properties of atmospheric air, which is regarded as a mechanical mixture of these gases.

* [*See Supplement*, p. 765.]

THE ATMOSPHERE.

According to the new and most careful determination of the weight of air by M. Regnault, 100 cubic inches of atmospheric air, deprived of aqueous vapour and the small quantity of carbonic acid it usually contains, weigh 30.82926 grains, at 60° and 30 Bar. Its density at the same temperature and pressure is estimated at 1000, and is conveniently assumed as the standard of comparison for the densities of gaseous bodies, as water is for solids and liquids. Hence, at 62°, air is 810 times lighter than water, and 11,000 times lighter than mercury. The bulk of air varies with its temperature and the pressure affecting it, according to the same laws as other gases (pages 40 and 81).[1]

The mean pressure of the atmosphere at the surface of the sea is generally estimated as equal to the weight of a column of mercury of 30 inches in height, which is about 15 pounds on the square inch of surface, and is equivalent to a column of water of nearly 34 feet in height. The oxygen alone is equal to a column of 7.8 feet of water over the whole earth's surface, from which an idea may be formed of the immense quantity of that element, and how small the effect must be of the oxidating processes observed at the earth's surface in diminishing it. If the atmosphere were of uniform density, its height, as inferred from the barometer, would be 11,000 times 30 inches, or 5.208 miles, but the density of air being proportional to the pressure upon it, diminishes with its elevation, the superior strata being always more rare and expanded than the inferior strata upon which they press.

DENSITY OF THE ATMOSPHERE.

Height above the sea in miles.	Volume.
0	1
2·705	2
5·41	4
8·115	8
10·82	16
13·424	32
16·23	64

At a height of 2.705 miles (11,556 feet) the atmosphere is of half density, by calculation, or one volume is expanded into 2, and the barometer would stand at 15 inches; the density is again halved for every 2.7 miles additional elevation. From calculations founded on the phenomena of refraction, the atmosphere is supposed to

---

[1] I. Weight of 1 Litre of Gases, at 0° C., Bar. 0.76 metre (Regnault).

	In Grammes.
Atmospheric Air	1.293187
Nitrogen	1.256167
Oxygen	1.429802
Hydrogen	0.089578
Carbonic Acid	1.977414

II. Weight of 100 Cubic Inches of Gases; Bar. 29.92 inches.

	At 32° F. In Grains.	At 60° F. In Grains.
Atmospheric Air	32.58684	30.82926
Nitrogen	31.66020	29.95260
Oxygen	36.13896	34.18979
Hydrogen	2.16216	2.04554
Carbonic Acid	50.03856	47.33972

Here the French litre is taken at 61.028 English cubic inches; the gramme at 15.4446 grains; and the volume of air and the other gases, at 60°, 1.05701, their volume at 32° being 1. (Regnault, Compt. Rend. t. 20, p. 975).

extend, in a state of sensible density, to a height of nearly 45 miles. It is certainly limited, probably from the expansibility of the aërial particles having a natural limit (page 81). The atmospheric pressure also varies at the same place, from the effect of winds and other causes, which are not fully understood. Hence the use of the barometer as a weather glass; for wet and stormy weather is generally preceded by a fall of the mercury in the barometer, and fair and calm weather by its rise.

The temperature of the atmosphere is greatest at the earth's surface, and has been observed to diminish one degree for every 352 feet of ascent, in the lower strata. It is believed, however, that the progressive diminution is less rapid at great distances from the earth. But at a certain height, the region of perpetual congelation is attained even in the warmest climates; the summits of the Andes, which rise 21,000 feet, being perpetually covered with snow under the equator. The line of perpetual congelation, which has been fixed at 15,207 feet at 0° latitude, descends progressively in higher latitudes, being 3,818 feet at 60°, and only 1,016 feet at 75°. The decrease of temperature with elevation in the atmosphere is ascribed to two causes. 1. To the property which air has of becoming cold by expansion, which arises from an increase of its latent heat with rarefaction. The actual temperature of the different strata of the atmosphere is indeed believed to be that due to their dilatation, supposing that they had all the same original temperature and density as the lowest stratum. 2. To the circumstance that the atmosphere derives its heat principally from contact with the earth's surface. The sun's rays appear to suffer little absorption in passing through the atmosphere; but there are some observations on the force of solar radiation which are not easily reconciled with that circumstance. A thermometer of which the bulb is blackened, rises a certain number of degrees above the temperature of the air, when exposed to the sun, but the rise is decidedly greater on high mountains than near the level of the sea, and in temperate, or even arctic climates, which is more remarkable, than within the tropics. It is a question how solar radiation is obstructed in the hotter climates (Daniell's Meteorological Essays, 2d edit.)

The blue colour of the sky has been found by Brewster to be due to light that has suffered polarization, which is therefore reflected light, like the white light of clouds. The air of the atmosphere must therefore have a disposition to absorb the red and yellow solar rays, and to reflect the blue rays. At great heights, the blue colour of the sky was observed by Theodore de Saussure to become deeper and deeper, being mixed with black, owing to the absence of white reflecting vapour or clouds. The red and golden tints of clouds appear to be connected with a remarkable property of steam observed by Professor J. Forbes. A light seen at night through steam issuing into the atmosphere from under a pressure of from 5 to 30 pounds on the inch, is found to appear of a deep orange red colour, exactly as if observed through a bottle containing nitrous acid vapour. The steam, when it possesses this colour, is mixed with air, and on the verge of condensation; and it is known that the golden hues of sunset depend upon a large proportion of vapour in the air, and are indeed a popular prognostic of rain (Phil. Mag. 3d ser. vol. xiv. pp. 121, 425, and vol. xv. pp. 25, 419.)

Winds. — The movement of masses of air, or wind, is always produced by inequality of temperature of the atmosphere at different points of the earth's surface, or in different regions of the atmosphere of equal elevation. The primary movement is always an ascending current, the heated and expanded air over some spot rising in a vertical column. Dense and colder air flows towards that point, producing the horizontal current which is remarked by an observer on the earth's surface. Some winds are of a very limited range, and depend upon local circumstances; such are the sea and land breeze experienced upon the coasts of tropical countries. From its low conducting power, the surface of the land is more quickly heated than the sea, so that soon after sunrise the expanded air over the former begins to ascend, and is replaced by colder air from the sea, forming the sea-breeze. But after sunset, the earth's heat, being less in quantity, is more quickly dissipated by radiation than that of the sea, and the air over the land becomes dense and flows outwards, displacing the air over the sea, and producing the land-breeze. It is obvious that these inferior currents must be attended by a superior current in an opposite direction, or that the air in these winds is carried in a perpendicular vortex of no great extent, of which the motion is reversed twice every twenty-four hours. A grand movement of a similar nature is produced in the atmosphere, from the high temperature of the equatorial compared with the polar regions of the globe; the air over the former constantly ascending, and having its place supplied by horizontal currents from the latter, within the lower region of the atmosphere. Hence, if the earth were at rest, the wind would constantly blow at its surface, from the poles to the equator, and in the opposite direction in the upper strata of the atmosphere. But the earth, accompanied by its atmosphere, makes a diurnal revolution upon its axis, in which any point on its surface is always passing to a point in space previously to the east of it, and with a velocity proportional to its circle of latitude on the globe; a velocity which is consequently nothing at the poles, and attains its maximum at the equator. The result of this is, that the lower current or polar stream, in tending to the equator, is constantly passing over parallels of latitude which have a greater degree of velocity of rotation to the east, than the stream itself, which comes thus to be felt as a resistance from the east; and instead of appearing as a wind directly from the north, as it really is, this stream appears as a wind from the east, with a certain northerly declination, which diminishes as the stream approaches the equator, where it flows directly from the east, constituting the great trade-wind which constantly blows across the Atlantic and Pacific Oceans from east to west within the tropics. Our keen east winds in spring have a low temperature, which attests their arctic origin. The upper or equatorial current has its course deflected by similar causes; starting from the equator it has a greater projectile force to the east than the parallels of latitude over which it has to pass, and retaining this motion towards the east it appears, as it passes over them, a west wind or wind from the west. The upper current, flowing in the opposite direction from the trade-wind below, was actually experienced by Humboldt and Bonpland on the summit of the Peak of Teneriffe, and has been indicated at various times by the transport of volcanic ashes by its means.

These currents, instead of flowing in a uniform manner over and under each other, appear often to descend, and to flow side by side, giving rise to hot and cold seasons in their different courses, and the great variability of climate of the temperate zone. On the great oceans, within the temperate zone, westerly winds prevail greatly over easterly, which are supposed by some to be the upper current descending to the surface of the earth. These westerly winds temper the climate of the western seaboard both of Europe and America, which is much milder than the climate of their eastern coasts.

The nature of the movement of the atmosphere in hurricanes has lately received considerable elucidation. It appears that they move in circles, and are great horizontal vortices, which are probably produced by currents of air meeting obliquely, like the little eddies or whirlwinds formed at the corner of streets. The whole vortex also travels, but its movement of translation is slow compared with its velocity of rotation (Colonel Reid on the Law of Storms; also the work of Mr. Espy).

Some hurricanes in the United States have a path of only a few hundred yards in width, but extending for many miles. An interesting theory of the origin of these, and many other local winds, has been proposed by Mr. Espy, and favourably reported upon by M. Babinet, to the French Institute. When a column of air, saturated with vapour at a high temperature, ascends in the atmosphere, it expands by the removal of pressure and becomes colder, as happens with dry air of the same temperature. But on being cooled to a certain point of temperature by its ascent, vapour condenses in the former, and raising the temperature of the column makes it specifically lighter and more buoyant. The ascent of damp air has thus a tendency to perpetuate itself, and may give rise to a most powerful upward aspiration, as is shown by calculation, quite adequate to prostrate trees, and produce the mechanical effects observed; the whole funnel being carried over the surface of the earth by a more general movement of the atmosphere.

Vapour. — The properties of the atmosphere are much affected by the presence of watery vapour in it, which it acquires from contact with the surface of the sea, lakes, rivers, and humid soil. The quantity which can rise into the air is limited by its temperature (page 90), and comes to be deposited again from various causes. The surface of the earth is cooled by radiation, and occasions the precipitation of dew from the air in contact with it. Vapour is also condensed into drops, from various agencies within the atmosphere itself. The following are the principal causes of clouds and rain. 1. The ascent of air in the atmosphere, and its consequent rarefaction, which is attended with cold. A cloud will be observed within the receiver of an air-pump, on the plate of which a little water has been spilt, on making two or three rapid strokes of the pump, which is due to this cause. It is observed in operation in the formation of the clouds and mists which settle on the summits of mountains. The wind passing over the surface of a level country is impeded by a mountain; rising in the atmosphere the stream overcomes the obstacle, and produces a cloud as it passes over the mountain, which appears stationary on its summit. 2. The mixing of opposite currents of hot and cold air, both saturated with humidity, may occasion rain, from the circumstance, first conjectured by Dr. Hutton, that the currents of air on mixing and attaining a mean temperature are incapable of sustaining the mean quantity of vapour. Thus, supposing equal volumes of air at 60° and 40°, both saturated with vapour, to be mixed, the tension of vapour at the former temperature being the 0.524th of an inch of mercury, and at the latter the 0.263d of an inch, the mean tension is 0.393d of an inch. But the tension of vapour at 50°, the intermediate temperature is only the 0.375th of an inch; and consequently the excess of the former tension, or vapour of the 0.018th of an inch of tension, must condense as rain. But this is an inconsiderable cause of rain compared with the next. 3. Contact of air in motion with the cold surface of earth, or mere proximity, appears to be the most usual cause of its refrigeration, and of the precipitation of rain from it. The mean temperature of January in this country is about 34°, but with a south-west wind the thermometer may be observed gradually to rise in the course of 48 hours to 54°. Now supposing this wind to be saturated with vapour at 54°, and to be cooled to 34°, as it is on its first arrival, the moisture which it must deposit is very considerable, as will appear by the following calculation: —

Tension of vapour at 54°	0.429	inch.
" " at 34°	0.214	"
Condensed	0.215	"

The mean annual fall of rain in London amounts to a column of 23 inches. The quantity collected by a rain-gauge is found to be affected to an extraordinary extent by very moderate differences of elevation. Thus the annual fall of rain in three situations was found, by Professor J. Phillips, to be as follows: —

	Inches.	Height.
Top of York Minster	15·910	242 feet.
Roof of Museum	20.461	73 "
Surface of ground	24.401	0 "

The last stated cause of rain throws some light on this inequality: the air is more cooled near the ground, and therefore deposits most humidity.

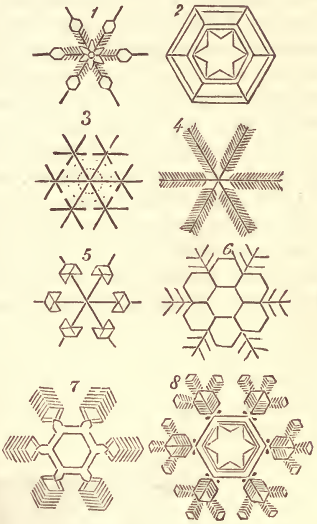
The annual fall is greater near the equator, and diminishes in high latitudes. At Granada (lat. 12° N.), it is 126 inches; at Calcutta (lat. 19° 46′), 81 inches; Rome, 39 inches; average of England, 31 inches; St. Petersburgh, 16 inches;

Uleaborg, 13½ inches. The number of rainy days follows a different proportion, the average during the year being about as follows:—

In Northern Europe	180
In Central Europe	146
In Southern Europe	120[1]

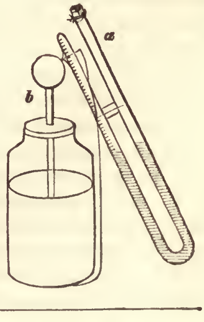
When clouds form at temperatures below 32°, the aqueous vapour is converted into an infinity of little needle-like crystals, which often diverge from each other at angles of 60° and 120°, as do also the thin crystals in freezing water. Snow differs very much in the arrangement of these spiculæ (fig. 112), but the flakes are all of the same configuration in the same storm. The figures are essentially referable to a hexagonal star or prism, one of the crystalline forms of ice. *Hail* is also produced by cold, but in circumstances which are entirely different. It occurs only in summer or in warm climates, and when the sun is above the horizon. It seems to be produced in a humid ascending current of air, greatly cooled by rarefaction, which has an upward velocity sufficient to sustain the falling hailstones at the same place till they attain considerable magnitude. The formation of hail is always attended with thunder or signs of electricity; and it has been found that small districts may be protected from its devastations by the elevation of many thunder rods.

Fig. 112.



Analysis of air.—A knowledge of the composition of the atmosphere followed that of its constituent gases. Various modes of analysis are practised:—1. A stick of phosphorus introduced into a known measure of air in a graduated tube, effects a complete absorption of the oxygen in 24 hours. On afterwards withdrawing the phosphorus the diminution of volume may be observed, which always indicates 20 or 21 per cent. of oxygen. 2. A known measure of air may be mixed with a slight excess of hydrogen more than sufficient to combine with its oxygen, 100 volumes of air, for example, with 50 volumes of hydrogen, and the mixture exploded in a strong glass tube of proper construction, by means of the electric spark. The diminution in volume of the gases after combustion is observed; and as oxygen and hydrogen unite in the exact ratio of one volume of the first to two volumes of the second, one-third of the diminution represents the volume of oxygen in the measure of air employed. The tube used for this purpose is called the voltaic eudiometer. The syphon eudiometer is a convenient instrument of this kind. It is formed of a straight tube moderately stout, of about 1-4th or 3-8ths of an inch internal diameter, sealed at one end, and about 22 inches long. The closed end of this tube being softened by heat, two stout platinum wires are thrust through the glass from opposite sides of the tubes, so that their extremities in the tube approach within one-tenth of an inch of each other. These are intended for the transmission of the electric spark, and are retained, as if cemented, in the apertures of the glass when the latter cools. One-half the tube next the closed end is afterwards graduated into hundredths of a cubic inch, and the tube is bent in the middle, like a syphon, as represented by *a* in the figure. By a little dexterity, a portion of the gaseous mixture to be exploded is

Fig. 113.



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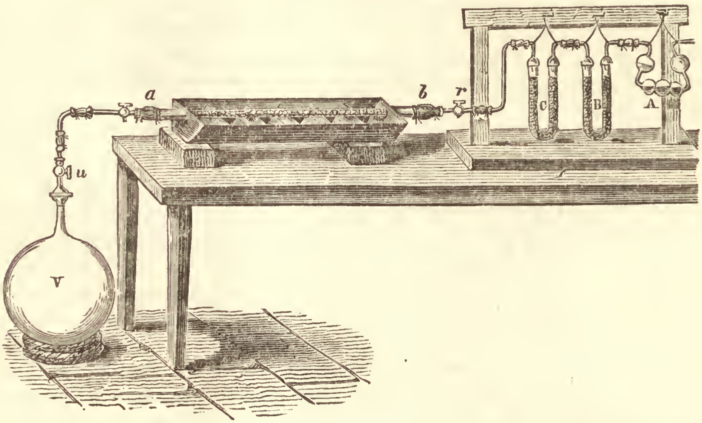
[1] See Müller's Physics and Meteorology, and Kämtz's Meteorology, by Walker.

transferred to the sealed limb of the instrument, at the water or mercurial trough, and the measure noted with the liquid at the same height in both limbs. The mouth of the open limb may then be closed by a cork, which can be fixed down by soft copper wire. A chain being now hung to one platinum wire, the other is presented to the prime conductor of an electric machine, or the knob of a charged Leyden phial *b*, so as to take a spark through the mixture, which is thereby exploded. The risk of the tube being broken by the explosion, which is considerable in the ordinary form of the eudiometer, is completely avoided in this instrument by the compression of the air retained by the cork in the open limb, this air acting as a recoil spring upon the occurrence of the explosion in the other limb. 3. The combustion of the mixed gases may be determined without explosion by means of a little pellet of spongy platinum, and the experiment can then be conducted over mercury in an ordinary graduated tube. 4. Another exact method of removing oxygen from air, recommended by Gay-Lussac, is the introduction into the air of slips of copper moistened with hydrochloric acid, which absorb oxygen with great avidity.

5. A solution in ammonia of the subchloride of copper, or of any salt of the suboxide of that metal, such as the sulphite, absorbs oxygen with great avidity, and may be used in the analysis of air.

6. In the recent careful analyses of air by MM. Dumas and Boussingault (Compt. Rend. 12, 1005) the oxygen was withdrawn, by passing air over reduced metallic copper at a red heat. To obtain the necessary precision in the results, the experiment was conducted in the following manner. In fig. 114, *a b* is a tube of the difficultly fusible or hard glass used in organic analysis, which is filled with metallic copper (reduced from the black oxide of copper by hydrogen), and placed in a long trough-furnace of sheet iron, in which it can be heated to redness throughout its whole length. The tube is provided with stopcocks at both ends, and attached by caoutchouc tubes to small glass tubes. By one of these small tubes it communicates with a glass balloon V, of about 1200 cubic inches in capacity, having a stopcock *u*; and by the other *r*, with a series of tubes A, B, and C. Of these A is a series of bulbs containing a concentrated solution of caustic potassa, and is intended for the absorption of the small portion of carbonic acid present in air; the U-shaped tube B contains fragments of pumice impregnated with the same alkaline solution; and the similar tube C is filled with pumice impregnated with oil of vitriol, in order to dry the air.

Fig. 114.



The balloon V is weighed and applied to the other apparatus in a vacuous state. The tube *a b* containing the metallic copper is also weighed beforehand. The tube and copper being heated to low redness, the stopcocks are partially opened, and air allowed to flow in a gradual manner into V. The oxygen is entirely absorbed by the copper, and the weight of that constituent ascertained by weighing the tube *a b* after the experiment. The nitrogen passes on alone into V, and its weight is found by again weighing that balloon. A great many analyses made in this way gave the following mean results:—

	Air by weight.	Air by volume.
Oxygen	23.10	20·90
Nitrogen	76.90	79.10
	100·00	100·00

Air from distant localities and different elevations has not exhibited any sensible variation in composition. [*See Supplement*, p. 762.]

The theory of the constitution of mixed gases of Dalton supposes that the oxygen and nitrogen of air form independent atmospheres, the one gas not pressing upon or interfering with the other. If each of these atmospheres were of uniform density, their heights would obviously be inversely as the densities of the two gases, the height of the nitrogen column 8, and that of the oxygen 7; and the proportion of the one gas to the other would vary with the elevation. The same variation should occur in the atmosphere in its actual state: the proportion being supposed 21 per cent. at the level of the sea, by a calculation on this principle it should be 20.070 per cent. at a height of 10,000 Parisian feet, and 19.140 per cent. at a height of 20,000 feet. But as the influence of the great polar and equatorial currents is allowed to extend to a greater height in the atmosphere than the last, and than has ever been reached by man, it is not to be wondered at that no diminution in the proportion of oxygen is observable in the accurate analyses of air from the summit of the Faulhorn (8000 feet) which were lately made by Brunner, with the view of testing this hypothesis. (Poggendorff, Handwörterbuch der Chemie, Bd. i. S. 570).

Besides these constituents, the atmosphere always contains a variable quantity of watery vapour and carbonic acid gas. The presence of the latter is observed by exposing to the air a bason of lime-water, which is soon covered by a pellicle of carbonate of lime. Its proportion is ascertained by adding baryta-water of a known strength, from a graduated pipette, to a large bottle of the air to be examined; agitating after each addition, till a slip of yellow turmeric paper is made permanently brown by the baryta-water after agitation, which proves that more of the latter has been added than is neutralized by the carbonic acid of the air. The carbonic acid is in the equivalent proportion (by weight) of the quantity of baryta which has been neutralized.

Another and perhaps more exact method is to draw a large but known volume of dry air through a U tube, containing pumice impregnated with caustic potassa, and to pass it afterwards through a second U tube, containing oil of vitriol. The increase of weight on both tubes weighed together is the proportion of carbonic acid.

Like every subject connected with the atmosphere, the proportion of carbonic acid which it contains was ably investigated by the Saussures. The elder philosopher of that name detected the presence of this gas in the atmosphere resting upon the perpetual snows of the summit of Mont Blanc, so that there can be no doubt that carbonic acid is diffused through the whole mass of the atmosphere. The younger Saussure has ascertained, by a series of several hundred analyses of air, that the mean proportion of carbonic acid is 4.9 volumes in 10,000 volumes of air, or almost exactly 1 in 2000 volumes; but it varies from 6.2 as a maximum to 3.7, as a minimum in 10,000 volumes. Its proportion near the surface of the earth is greater in summer than in winter, and during night than during day upon an average of many observations. It is also rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; a distribution of this gas which proves that the action of vegetation at the surface of the earth is sufficient to keep down the proportion of it in the atmosphere, within a certain limit. (Saussure, Ann. de Chim. et de Phys. t. xxxviii. p. 411; and t. xliv. p. 5). An enormous quantity of carbonic acid is discharged from the elevated cones of the active volcanoes of America, according to the observations of Boussingault, which may partly account for the high proportion of that gas in the upper regions of the atmosphere. The gas emitted from the volcanoes of the old world, according to Davy and others, is principally nitrogen.

Carbonic acid is a constituent of the atmosphere which is essential to vegetable life, plants absorbing that gas, and deriving from it the whole of their carbon. Extensive forests, such as those of the Landes in France, which grow upon sands absolutely destitute of carbonaceous matter, can obtain their carbon in no other manner. But the oxygen of the carbonic acid is not retained by the plant, for the lignin and other constituent principles of vegetables, contain, it is well known, no more oxygen than is sufficient to form water with their hydrogen, and which, indeed, has entered the plant as water. The oxygen of the carbonic acid must therefore be returned in some form to the atmosphere. The discharge of pure oxygen gas from the leaves of plants was first observed by Priestley, and the general action of plants upon the atmosphere has subsequently been minutely studied by Sir H. Davy and Dr. Daubeny. The decomposition of carbonic acid requires the concurrence of light; and is not therefore sensible during the night. That plants fully compensate for the loss of oxygen occasioned by the respiration of animals and other natural processes is not improbable; but the mass of the atmosphere is so vast that any change in its composition must be very slowly effected. It has, indeed, been estimated that the proportion of oxygen consumed by animated beings in a century does not exceed 1-7200th of the whole quantity.

Other gases and vaporous bodies are observed to enter the atmosphere, but none of them can afterwards be detected in it, with the exception of hydrogen in some form, probably as the light carburetted hydrogen of marshes, of which Boussingault believes that he has been able to detect the presence of a minute but appreciable proportion. (Ann. de Chim. et de Phys. lvii. 148). He also observed concentrated sulphuric acid to be blackened when exposed in a glass capsule to the air, protected from dust, and at a distance from vegetation, which he ascribes to the occasional presence in the air of some volatile carbonaceous compound which is absorbed and decomposed by the acid.

Ammonia (NH_3) also is a minute but essential constituent of air, probably in the form of carbonate. It is brought down by rain, and is the principal source of the nitrogen of plants.

Omitting the aqueous vapour always present in air, but of which the proportion is constantly fluctuating, it may be represented as follows, in 10,000 volumes:—

COMPOSITION OF DRY AIR BY VOLUME.

Nitrogen	7912
Oxygen	2080
Carbonic acid	4
Carburetted hydrogen (CH_2)	4
Ammonia	Trace
	10,000

Of the odoriferous principles of plants, the miasmata of marshes and other matters of contagion, the presence, although sufficiently obvious to the sense of smell, or by their effects upon the human constitution, cannot be detected by chemical tests. But it may be remarked in regard to them, that few or none of the compound volatile bodies we perceive entering the atmosphere, could long escape destruction from oxidation. The atmosphere contains, indeed, within itself, the means of its own purification, and slowly but certainly converts all organic substances exposed to it into simpler forms of matter, such as water, carbonic acid, nitric acid, and ammonia. Although the occasional presence of matters of contagion in the atmosphere is not to be disputed, still it is an assumption, without evidence, that these substances are volatile or truly vaporous. Other matters of infection with which we can compare them, such as the matter of cow-pox, may be dried in the air, and are not in the least degree volatile. Indeed, volatility of a body implies a certain simplicity of constitution and limit to the number of atoms in its integrant particle, which true organic bodies appear not to possess. Again, the source of such bodies being at all times inconsiderable, they would, if vapours, be liable to a speedy attenuation by diffusion so great as to render their action wholly inconceivable. It is more probable that matters of contagion are highly organized particles of fixed matter, which may find its way into the atmosphere, notwithstanding, like the pollen of flowers, and remain for a time suspended in it; a condition which is consistent with the admitted difficulty of reaching and destroying those bodies by gaseous chlorine, and with the washing of walls and floors as an ordinary disinfecting practice. On this obscure subject, I may refer to a valuable paper by the late Dr. Henry upon the application of heat to disinfection, in which it is proved that a temperature of 212° is destructive to such contagious matters as could be made the subject of experiment. (Phil. Mag. 2d ser., vols. x. p. 363; xi. pp. 22, 207 (1832).

With reference to gaseous disinfectants, it may be remarked that sulphurous acid gas (obtained by burning sulphur) is preferable, on speculative grounds, to chlorine. No agent checks more effectually the first development of animal or vegetable life. This it does by preventing oxidation. In the same manner it renders impossible the first step in putrefactive decomposition and fermentation. All animal odours and emanations are most immediately and effectively destroyed by it. The fœtid odour from the boiling solution of cochineal (for instance), which is so persistent in dye-houses, is most completely removed by the admission of sulphurous acid vapour (J. Graham).

The compounds of nitrogen or oxygen are the following: —

Protoxide of nitrogen or nitrous oxide	NO
Binoxide of nitrogen or nitric oxide	NO_2
Nitrous acid	NO_3
Peroxide of nitrogen (hyponitric acid of Thenard)	NO_4
Nitric acid	NO_5

PROTOXIDE OF NITROGEN.

Syn. PROTOXIDE OF AZOTE, NITROUS OXIDE; *Eq.* 22 *or* 275; NO; *density* 1520·4; ☐☐.

This gas was discovered by Dr. Priestley about 1776, and studied by Davy, whose "Researches, Chemical and Philosophical," published in 1809, contain an elaborate investigation of its properties and composition. Davy first observed the stimulating power of nitrous oxide when taken into the lungs, a property which has since attracted a considerable degree of popular attention to this gas.

*Preparation.**—Protoxide of nitrogen is always prepared from the nitrate of ammonia. Some attention must be paid to the purity of that salt, which should contain no hydrochlorate of ammonia. It is formed by adding pounded carbonate of ammonia to pure nitric acid, which, if concentrated, may be previously diluted with half its bulk of water, so long as there is effervescence; and a small excess of the carbonate may be left at the end in the liquor. The solution should be filtered, and concentrated till its boiling point begins to rise above 250°, and a drop of it becomes solid on a cool glass plate. On cooling, it forms a solid cake, which may be broken into fragments. To obtain nitrous oxide, a quantity of this salt, which should never be less than 6 or 8 ounces, is introduced into a retort, or a globular

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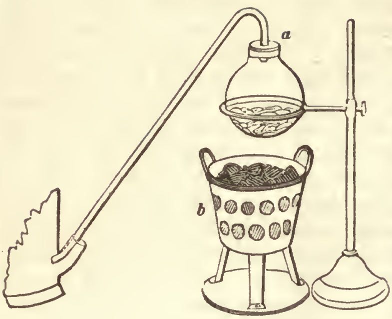
* [*See Supplement*, p. 766.]

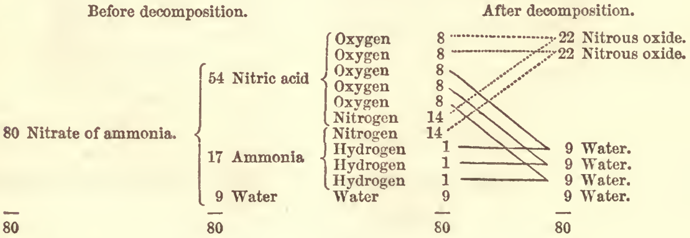
FIG. 115.



flask, called a bolt-head *a*, and heated by a charcoal choffer *b*, the diffused heat of which is more suitable than the heat of a lamp. Paper may be pasted over the cork of the bolt-head to keep it air-tight. At a temperature not under 340° the salt boils and begins to undergo decomposition, being resolved into nitrous oxide and water. As heat is evolved in this decomposition, which is a kind of combustion or deflagration, the choffer must be withdrawn to such a distance from the flask as to sustain only a moderate ebullition. If the temperature is allowed to rise too high, the ebullition becomes tumultuous, and the flask is filled with white fumes, which have an irritating odour; and the gas which then comes off is little more than nitrogen. Nitrous oxide should be collected in a gasometer or in a gas-holder filled with water of a temperature about 90°, as cold water absorbs much of this gas. The whole salt undergoes the same decomposition, and nothing whatever is left in the retort.[1]

Nitrous oxide is likewise produced when the salt called nitro-sulphate of ammonia is thrown into an acid; and also when zinc and tin are dissolved in dilute nitric acid, but the latter processes do not afford the gas in a state of purity.

The nature of the decomposition of the nitrate of ammonia will be best explained by the following diagram, in which an equivalent of the salt, or 80 parts, is supposed to be used. It will be observed that the three equivalents of hydrogen in the ammonia are burned, or combine with three equivalents of the oxygen of the nitric acid, and form water, while the two equivalents of nitrogen in the ammonia and nitric acid combine with the two remaining equivalents of the oxygen of the latter:—



Or in symbols:—

$$NH_3, HO+NO_5=2NO \text{ and } 4HO.$$

From the diagram it appears that 80 grains of the salt yield 44 grains of nitrous oxide and 35 grains of water. One grain of salt yields rather more than one cubic inch of gas.

Properties.—Nitrous oxide possesses the usual mechanical properties of gases, and has a faint agreeable smell. It has been liquefied by evolving it from the decomposition of the nitrate of ammonia in a sealed tube, and possessed in the liquid state an elastic force of above 50 atmospheres at 45°. [It has also been liquefied by mechanical compression (Natterer, Ann. de Phar. 54, 254). Liquid nitrous oxide is colourless, very volatile, boils under the pressure of one atmosphere at

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[1] For the preparation and properties of this and other gases, the Elements of Chemistry (1829) of the late Dr. Henry may still be consulted with advantage.

—125° (Regnault, Compt. Rend. t. 28, 333): a drop falling on the hand produces effects similar to a burn; potassium, charcoal, sulphur, and phosphorus float on its surface unaltered, but ignited charcoal burns with brilliancy. Water poured on it, freezes instantly, and the liquid is converted into gas with almost explosive rapidity. Issuing from a jet pipe, part is reduced to a solid state by the sudden evaporation of the rest. The solid is snowlike, and placed on the hand produces the same effects as the liquid (Dumas, Compt. Rend. t. 27, 463). When the liquid is exposed to the cold produced by the vaporization of solid carbonic acid and ether, it freezes at the temperature of —150° (Faraday).—R. B.] The gas is formed by the union of a combining measure, or 2 volumes of nitrogen, with a combining measure, or 1 volume of oxygen, which are condensed into 2 volumes, the combining measure of this gas. The weight of a single volume, or the density of the gas, is therefore by calculation —

$$\frac{971.4 + 971.4 + 1105.6}{2} = 1524.2$$

Cold water agitated with this gas dissolves about three-fourths of its volume of the gas, and acquires a sweetish taste, but, I believe, no stimulating properties. Bodies which burn in air, burn with increased brilliancy in this gas, if introduced in a state of ignition. A newly blown out taper with a red wick may be rekindled in it, as in oxygen. Mixed with an equal bulk of hydrogen, and ignited by flame and the electric spark, it detonates violently. In all these cases of combustion, the nitrous oxide is decomposed, its oxygen uniting with the combustible and its nitrogen being set free. When transmitted through a red-hot porcelain tube, nitrous oxide is likewise decomposed and resolved into oxygen, nitrogen, and the peroxide of nitrogen.

Nitrous oxide was supposed by Davy to combine with alkalies, when generated in contact with them, but these compounds have since been found to contain nitrosulphuric acid.

This gas may be respired for two or three minutes without inconvenience, and when the gas is unmixed with air, and the lungs have been well emptied of air before respiring, it induces an agreeable state of reverie or intoxication, often accompanied with considerable excitement, which lasts for a minute or two, and disappears without any unpleasant consequences. The gas from an ounce and a half or two ounces of nitrate of ammonia is sufficient for a dose, and it should be respired from a bag of the size of a large ox-bladder, and provided with a wooden tube of an inch internal diameter. The volume of the gas diminishes rapidly during the inspiration, and finally only a few cubic inches remain. An animal entirely confined in this gas soon dies from the prolonged effects of the intoxication.

BINOXIDE OF NITROGEN.

Syn. BINOXIDE, OR DEUTOXIDE OF AZOTE, NITRIC OXIDE; *Eq.* 30 or 375;

NO_2; *density* 1038·8; .

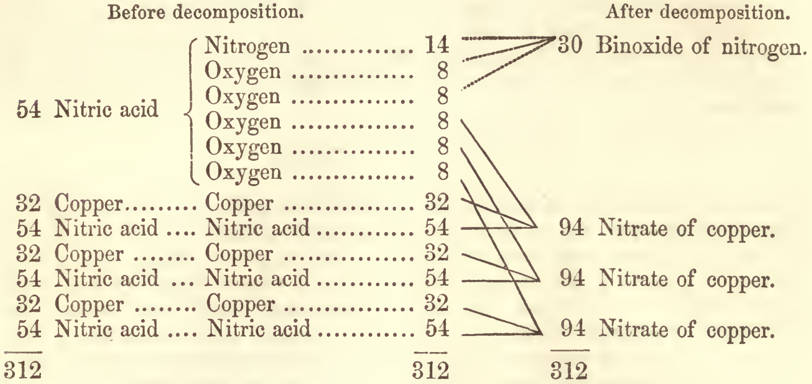
This gas, which comes off during the action of nitric acid upon most metals, appears to have been collected by Dr. Hales, the father of pneumatic chemistry, but its properties were first minutely studied by Dr. Priestley.

*Preparation.**—Binoxide of nitrogen is easily procured by the action of nitric acid diluted to the specific gravity 1.2, upon sheet copper clipped into small pieces. As no heat is required, this gas may be evolved like hydrogen from a gas bottle (page 234). Mercury may be substituted for copper, but it is then necessary to apply a gentle heat to the materials. This gas may be collected and retained over water without loss.

* [*See Supplement, p.* 766.]

In dissolving in nitric acid, the copper takes oxygen from one portion of acid and becomes oxide of copper, which combines with another portion of acid, and forms the nitrate of copper, the solution of which is of a blue colour. The portion of nitric acid which is decomposed losing three equivalents of oxygen and retaining two, appears as nitric oxide gas. This is more clearly shown in the following diagram:—

ACTION OF NITRIC ACID UPON COPPER.



Or in symbols:—

$$4NO_5 \text{ and } 3Cu = 3(Cu\,O,\ NO_5) \text{ and } NO_2.$$

Properties.—This gas is colourless, but when mixed with air it produces ruddy fumes of the peroxide of nitrogen. It is irritating, and causes the glottis to contract spasmodically when an attempt is made to respire it. Nitric oxide has never been liquefied: water at 60°, according to Dr. Henry, takes up only 5 or 6 per cent. of this gas. It is formed of one combining measure of nitrogen or 2 volumes, and two combining measures of oxygen or 2 volumes, united without condensation, so that the combining measure of nitric oxide contains 4 volumes. The weight of one volume, or the density of the gas, is therefore

$$\frac{971.4+971.4+1105.6+1105.6}{4}=1038.5.$$

This gas is not decomposed by a low red heat.

Many combustibles do not burn in nitric oxide, although it contains half its volume of oxygen. A lighted candle and burning sulphur are extinguished by it; mixed with hydrogen, it is not exploded by the electric spark or by flame, but it imparts a green colour to the flame of hydrogen burning in air. Phosphorus and charcoal, however, introduced in a state of ignition into this gas, continue to burn with increased vehemence. The state of combination of the oxygen in this gas appears to prevent that substance from uniting with combustibles, unless, like the two last mentioned, they evolve so much heat as to decompose the nitric oxide. Several of the more oxidable metals, such as iron, withdraw the half of the oxygen from this gas, when left in contact with it, and convert it into nitrous oxide.

No property of nitric oxide is more remarkable than its attraction for oxygen, and it may be employed to separate this from all other gases. Nitric oxide indicates the presence of free oxygen in a gaseous mixture, by the appearance of fumes which are pale and yellow with a small, and reddish brown and dense with a large proportion of the latter gas; and also by a subsequent contraction of the gaseous volume, arising from the absorption of these fumes by water. Added in sufficient quantity, nitric oxide will thus withdraw oxygen most completely from any mixture. But notwithstanding this property, nitric oxide cannot be employed with advantage in the analysis of air or similar mixtures, for the contraction which it occasions does not afford certain data for determining the proportion of oxygen which has disappeared. Nitric oxide is capable of combining with different proportions of oxygen, a combining measure or 4 volumes of the gas uniting, in such experiments, with 1, 2 or 3 volumes of oxygen, and forming nitrous acid, peroxide of nitrogen or nitric acid, or several of these compounds at the same time.

This oxide of nitrogen, like the preceding, is a neutral body, and has a very limited range of affinity. A substance is left on igniting the nitrate of potassa or baryta, which was supposed to be a compound of nitric oxide with potassium, or barium, but Mitscherlich finds it to be either the caustic protoxide itself or the peroxide of the metal. But nitric oxide is absorbed by a solution of the sulphate of iron, which it causes to become black; the greater part of the gas may be expelled again by boiling the solution. All the soluble proto-salts of iron have the same property, and the nitric oxide remains attached to the oxide of iron when precipitated in the insoluble salts of that metal. The proportion of nitric oxide in these combinations is found by Peligot to be definite; one eq. of the nitric oxide to four of the protoxide of iron; or, the nitric oxide contains the proportion of oxygen required to convert the protoxide into sesquioxide of iron. (Ann. de Chim. et de Phys. t. liv. p. 17). Nitric oxide is also absorbed by nitric acid. With sulphurous acid nitric oxide forms a compound which will be more particularly noticed under that acid.

NITROUS ACID.

Syn. AZOTOUS ACID (*Thenard*). *Eq.* 38 or 475; NO_3.

The direct mode of forming this compound is by mixing 4 volumes of binoxide of nitrogen with 1 volume of oxygen, both perfectly dry, and exposing the mixture to a great degree of cold. The gases unite, and condense into a liquid of a green colour, which is very volatile, and forms a deep reddish yellow coloured vapour. Nitrous acid prepared in this way is decomposed at once when thrown into water; an effervescence occurring, from the escape of nitric oxide, and nitric acid being produced, which gives stability to a portion of the nitrous acid. Nitrous acid cannot be made to unite directly with alkalies and earths, probably owing to the action of water first described. But when oxygen gas is mixed with a large excess of nitric oxide, in contact with a solution of caustic potassa, the gases were found by Gay-Lussac always to disappear in the proportions of nitrous acid, which was produced and entered into combination with the potassa, forming a *nitrite* of potassa. Similar nitrites may also be produced by calcining the nitrate of soda till the fused salt becomes alkaline; or by boiling the nitrate of lead with metallic lead. The nitrite of soda may be dissolved and filtered, and the solution precipitated by nitrate of silver; a process which gives the nitrite of silver, a salt possessing a sparing degree of solubility, like that of cream of tartar, but which may be purified by solution and crystallization, and then affords ready means of obtaining the other nitrites by double decomposition (Mitscherlich). Nitrous acid is liberated from the nitrites by acetic acid. When free sulphuric acid is added to a solution of nitrite of silver, the disengaged nitrous acid is immediately resolved into nitric acid and nitric oxide. The subnitrite of lead, on the other hand, may be decomposed by the bisulphate of potassa or soda to obtain a neutral nitrite of one of these bases (Berzelius). The nitrites of potassa and soda are soluble in alcohol, while the nitrates are not so.

Nitrous acid is also capable of combining with several acids, in particular with iodic, nitric, and sulphuric acids. Its combination with the last is obtained by sealing up together liquid sulphurous acid and peroxide of nitrogen (NO_4) in a glass tube. In the course of a few days the tube may be opened: the substances are combined, and form a solid mass, which may be heated up to (200° C.) its point of fusion. At a higher temperature it distils without alteration. In this experiment, sulphurous acid acquires an equivalent of oxygen, and becomes sulphuric acid.

while peroxide of nitrogen loses an equivalent of oxygen, and becomes nitrous acid, but one half only of the latter acid formed unites with sulphuric acid, the composition of the body formed being NO_3+2SO_3. The reaction is expressed as follows:—

$$2SO_3 \text{ and } 2NO_4=NO_3+2SO_3 \text{ and } NO_3.$$

This compound is soluble in strong oil of vitriol without decomposition; but from sulphuric acid somewhat diluted it takes water, and forms a crystalline substance, which often appears in the manufacture of sulphuric acid, as we shall afterwards find. The original solid compound is decomposed by pure water or highly diluted sulphuric acid, and the sulphuric and nitrous acids become free. The tendency of nitrous acid to combine with other acids has already been noticed, as assimilating this compound of nitrogen to arsenious acid and the oxide of antimony (page 147).

PEROXIDE OF NITROGEN.

Syn. HYPONITRIC ACID, NITROUS GAS (*Berzelius*). *Eq.* 46 *or* 575; NO_4; *theoretical density*, 1591.3;

This compound forms the principal part of the ruddy fumes which always appear on mixing nitric oxide with air. As it cannot be made to unite either directly or indirectly with bases, and has no acid properties, any designation for this oxide of nitrogen which implies acidity should be avoided, and the name nitrous acid in particular, which is applied on the continent to the preceding compound. The name peroxide of nitrogen is more in accordance with the rules generally followed in naming such compounds.

Preparation.—When 4 volumes of nitric oxide and 2 of oxygen, both perfectly dry, are mixed, this compound is alone produced, and the six volumes of mixed gases are condensed into 4 volumes, which may be considered the combining measure of peroxide of nitrogen. The weight of 1 volume, or the density of this gas, must therefore be

$$\frac{1038.5\times4+1105.6\times2}{4}=1591.3.$$

The peroxide of nitrogen is also contained in the coloured and fuming nitric acid of commerce, and may be obtained in the liquid condition by gently warming that acid, and condensing the vapour which comes over, by transmitting it through a glass tube surrounded by ice and salt. But it is prepared with most advantage from the nitrate of lead, the crystals of which, after being pounded and well dried, to deprive the salt of hygrometric water, are distilled in a retort of hard glass, or porcelain, at a red heat, and the red vapours condensed in a receiver kept very cold by a freezing mixture. Oxygen gas escapes during the whole process, the nitric acid of the nitrate of lead being resolved into oxygen and peroxide of nitrogen; or $NO_5=NO_4$ and O. As obtained by the last process, which was proposed by Dulong, peroxide of nitrogen is a highly volatile liquid, boiling at 82°, of a red colour at the usual temperature, orange yellow at a lower temperature, and nearly colourless below zero, of density 1·451, and a white solid mass at —40°. It is exceedingly corrosive, and, like nitric acid, stains the skin yellow. The red colour of its vapour becomes paler at a low temperature, but with heat increases greatly in intensity, so as to appear quite opaque when in a considerable body at a high temperature. It is the vapour which Brewster observed to produce so many dark lines in the spectrum of a ray of light which passes through it (page 100). The peroxide is not decomposed by a low red heat, and appears to be the most stable of the oxides of nitrogen. No compound of it is known, unless peroxide of nitrogen be the radical, as some suppose, of nitric acid. But Berzelius is inclined to consider this oxide as itself a compound of nitric and nitrous acids, for

$$NO_5+NO_3=2NO_4.$$[1]

The liquid peroxide of nitrogen is partially decomposed by water, nitric oxide coming off with effervescence, and more and more nitric acid being produced, in proportion to the quantity of water added; but a portion of the peroxide always escapes this action, being protected by the nitric acid formed. In the progress of this dilution the liquid undergoes several changes of colour, passing from red to yellow, from that to green, then to blue, and becoming at last colourless. The peroxide of nitrogen is readily decomposed by the more oxidable metals, and is a powerful oxidizing agent.

NITRIC ACID.

Syn. AZOTIC ACID (*Thenard*). *Eq.* 54 *or* 675; NO_5.

A knowledge of this highly important acid has descended from the earliest ages of chemistry, but its composition was first ascertained by Cavendish, in 1785. He succeeded in forming nitric acid from its elements, by transmitting a succession of electric sparks during several days through a small quantity of air, or through a mixture of 1 volume of nitrogen and 2½ volumes of oxygen, confined in a small tube over water, or over solution of potassa; in the last case, the absorption of the gases was complete, and nitrate of potassa was obtained. A trace of this acid in combination with ammonia has been detected in the rain of thunder-storms, produced probably in the same manner. It was also observed by Gay-Lussac to be the sole product when nitric oxide is added, in a gradual manner, to oxygen in excess over water; the gases then unite, and disappear in the proportion of 4 volumes of the former to 3 of the latter. It is also a constituent of the salt, nitre or salpetre, found in the soil of India and Spain, which is a nitrate of potassa, and also of nitrate of soda, which occurs in large quantities in South America.

[Anhydrous nitric acid was first prepared in 1849, by M. Deville (Compt. Rend. t. 28, p. 257), by treating dry nitrate of silver with dry chlorine. The nitrate of silver is placed in a U-tube, to which a second, having a spherical reservoir at the curved part, is attached. The first tube is immersed in a vessel of water, which can be heated by a spirit-lamp, and the second in a freezing mixture. Chlorine gas is evolved and passed first through a tube containing chloride of calcium, then another filled with pumice moistened with sulphuric acid, that it may be perfectly dried before it reaches the nitrate of silver. All the joints are united by the blow-pipe. The nitrate of silver is heated to 356° F., and a stream of carbonic acid passed through the apparatus to dry the salt, after which it is allowed to cool and the chlorine is transmitted. At common temperatures there is no appearance of action, but when the heat is raised to 203 and then lowered to between 135 and 155°, decomposition takes place, chloride of silver is produced, and crystals of nitric acid begin to appear in the second U-tube at the part not immersed in the freezing mixture, and a small quantity of liquid condenses in the spherical reservoir, while oxygen and chlorine gases escape. To transfer the nitric acid, the stream of chlorine is replaced by carbonic acid, and the freezing mixture taken away; the liquid is now removed from the reservoir and a bulb attached to receive the anhydrous acid. This bulb is immersed in the freezing mixture, and the acid evaporating at ordinary temperature condenses in the bulb, which when filled is to be sealed by the blowpipe.

Properties.— Anhydrous nitric acid forms transparent colourless crystals, belonging to the right rhombic system. It fuses at a little above 85°, and boils about

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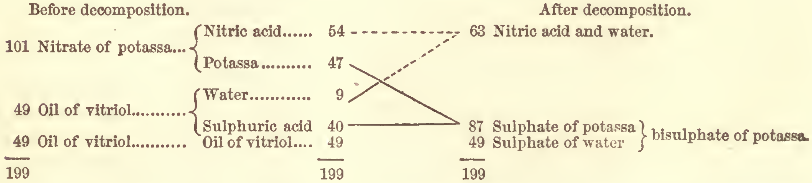
[1] Traité de Chimie, par J. J. Berzelius, traduite par MM. Esslinger et Hoeffer, Didot, Paris, 1845. An excellent edition of this most valuable system of chemistry.

113°, decomposing slightly at that temperature. In contact with water, it dissolves with the evolution of much heat.

At ordinary temperatures it is liable to spontaneous decomposition, and bursts the bulb by the increased tension of the confined gases (Dumas, Compt. Rend. t. 28, p. 323): — R. B.] [*See Supplement*, p. 766.]

Preparation. — This acid has not until recently been obtained in an insulated state, but in combination with water, as in aqua fortis or the hydrate of nitric acid, or with a fixed base, as in the ordinary nitrates. The hydrate, (which is popularly termed nitric acid,) is eliminated from nitrate of potassa by means of oil of vitriol, which is itself a hydrate of sulphuric acid. That acid unites with potassa, in this decomposition, and forms sulphate of potassa, displacing nitric acid, which last brings off in combination with itself the water of the oil of vitriol. There is a great advantage, first pointed out by Mr. Phillips, in using two equivalents of oil of vitriol to one of nitrate of potassa, which is 98 of the former to 101 of the latter, or nearly equal weights. The acid and salt, in these proportions, are introduced into a capacious plain retort, provided with a flask as a receiver. Upon the application of heat, a little of the nitric acid first evolved undergoes decomposition, and red fumes appear, but soon the vapours become nearly colourless, and are easily condensed in the receiver. During the whole distillation, the temperature need not exceed 260°. The mass remains pasty till all the nitric acid is disengaged, and then enters into fusion; red vapours again appearing towards the end of the process. The residuary salt is the bisulphate of potassa, or double sulphate of water and potassa, $HO.SO_3 + KO.SO_3$. The rationale of this important process is exhibited in the following diagram: —

PROCESS FOR NITRIC ACID.



In this operation twice as much sulphuric acid is employed as is required to neutralize the potassa of the nitre, by which means the whole nitric acid is eliminated without loss at a moderate temperature, and a residuary salt is left which is easily removed from the retort.

With half the preceding quantity, or a single equivalent of oil of vitriol, the materials in the retort are apt to undergo a vesicular swelling, upon the application of heat, and to pass into the receiver. Abundance of ruddy fumes are also evolved, that are not easily condensed, and prove that the nitric acid is decomposed. The temperature in this process must also be raised inconveniently high towards the end of the operation, in order to decompose the whole nitre. The peculiarities of the decomposition here arise from the formation of bisulphate of potassa in the operation, the whole sulphuric acid uniting in the first instance with half the potassa of the nitre. Now, it is only at an elevated temperature that the acid salt thus formed can decompose the remaining nitre; — a temperature which is sufficient to decompose nitric acid, as may be proved by transmitting the vapour of the concentrated acid through a tube heated to the same degree.

Ordinary nitric acid for manufacturing purposes is generally prepared by distilling nitrate of soda with an equivalent of sulphuric acid not at its highest degree of concentration in a large cylinder of cast iron (fig. 116, page 261), supported in brickwork over a fire. Both ends of the cylinder are moveable, and generally consist of circular discs of stone. The nitric acid which distils over is condensed in a

FIG. 116.

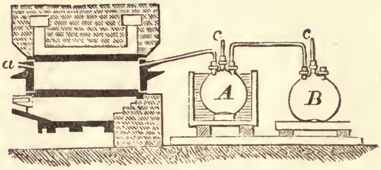
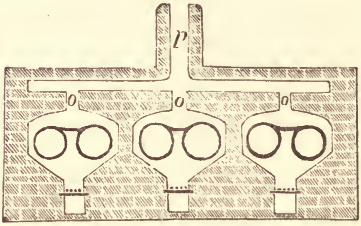


FIG. 117.



series of large vessels of salt-glaze ware, of the form of Woulf bottles, of which two, A, B, are shown in the figure.

The iron cylinders are generally so supported that two of them are heated by one fire, as in fig. 117, which is a sectional view of three pairs of such retort cylinders. The iron of the vault or roof of the cylinder is most apt to be corroded by the acid vapours, and is therefore protected by a coating of fire-clay or of tiles of the same material cemented together.

Properties. — The acid prepared by the first process is colourless, or has only a straw yellow tint. If the oil of vitriol has been in its most concentrated condition, which is seldom the case, the nitric acid is in its state of highest concentration also, and contains no more than a single equivalent of water. The density of this acid is 1.522 at 58°; but a slight heat disengages a little peroxide of nitrogen from it, and its density becomes 1.521 (Mitscherlich). The density of the strongest colourless nitric acid which Mr. Arthur Smith could prepare was 1.517 at 60°; it boiled at 184°, and came within 1 per cent. of the protohydrate in composition (Chem. Mem. iii. 402). When distilled, it is partially decomposed by the heat, and affords a product of a strong yellow colour. Its vapour transmitted through a porcelain tube, heated to dull redness, is decomposed in a great measure into oxygen and peroxide of nitrogen; and into oxygen and nitrogen gases, when the tube is heated to whiteness. The colourless liquid acid becomes yellow, when exposed to the rays of the sun, and on loosening the stopper of the bottle it is sometimes projected with force, from the state of compression of the disengaged oxygen. Hence to preserve this acid colourless it must be kept in a covered bottle. It congeals at about —40°, but diluted with half its weight of water, it becomes solid at 1½°, and with a little more water its freezing point is again lowered to —45°. Exposed to the air, the concentrated acid fumes, from the condensation by its vapour of the moisture in the atmosphere. It also attracts moisture from damp air, and increases in weight; and when suddenly mixed with 3-4ths of its weight of water, may rise in temperature from 60° to 140°.

Nitric acid has a great affinity for water, and diminishes in density with the proportion of water added to it. A table has been constructed in which the per centage of absolute acid is expressed in mixtures of various densities, which is useful for reference and will be given in an appendix. There appears to be no definite hydrate of this acid between the first (the nitrate of water), and that containing 3 eq. of water additional (A. Smith). The first has no action upon tin or iron The second is acid of density 1.424, which therefore contains 4 eq. of water. This last hydrate was found by Dr. Dalton to have the highest boiling point of any hydrate of nitric acid: it is 250°, and both weaker and stronger acids are brought to this strength by continued ebullition, the former losing water and the latter acid. The density of the vapour of this hydrate is found to be 1243 by A. Bineau, and it contains 2 volumes of nitrogen, 5 volumes of oxygen, and 8 volumes of steam condensed into 10 volumes, which are therefore the combining measure of this vapour (Ann. de Chim et de Phys. lxviii. p. 418).

Nitric acid is exceedingly corrosive, and one of the strongest acids, yielding only in that respect to sulphuric acid. The facility with which it parts with its oxygen renders it very proper for oxidating bodies in the humid way, a purpose for which it is constantly employed. Nearly all the metals are oxidized by means of it; some of them with extreme violence, such as copper, mercury, and zinc, when the concentrated acid is used; and tin and iron by the acid very slightly diluted. Poured upon red-hot charcoal, it causes a brilliant combustion. When mixed with a fourth of its bulk of sulphuric acid, and thrown upon a few drops of oil of turpentine, it occasions an explosive combustion of the oil. Sulphur digested in nitric acid at the boiling point is raised to its highest degree of oxidation and becomes sulphuric acid; iodine is also converted by it into iodic acid. Most vegetable and animal substances are converted by nitric acid into oxalic and carbonic acids. It stains the cuticle and nails of a yellow colour, and has the same effect upon wool; the orange patterns upon woollen table-covers are produced by means of it. In the undiluted state it forms a powerful cautery.

In acting upon the less oxidable metals, such as copper and mercury, nitric acid is itself decomposed, and nitric oxide gas produced, which comes off with effervescence. Palladium and silver, when they are dissolved by the acid in the cold, produce nitrous acid in the liquor and evolve no gas, but this is very unusual in the solution of metals by nitric acid. Those metals, such as zinc, which are dissolved in diluted acids with the evolution of hydrogen, act in two ways upon nitric acid; sometimes they decompose it, so as to disengage a mixture of peroxide of nitrogen and nitric oxide, and at other times they decompose both water and nitric acid at once, in such proportions that the hydrogen of the water combines with the nitrogen of the acid to form ammonia, which last combines with another portion of acid, and is retained in the liquor as nitrate of ammonia. The protoxide of nitrogen is also evolved when zinc is dissolved in very feeble nitric acid, which may arise from the action of hydrogen upon nitric oxide. Nitric acid, in its highest state of concentration, exerts no violent action upon certain organic substances, such as lignin or woody fibre and starch, for a short time, but unites with them and forms singular compounds. A proper acid for such experiments is procured with most certainty by distilling 100 parts of nitre, with no more than 60 parts of the strongest oil of vitriol. If paper is soaked for one minute in such an acid, and afterwards washed with water, it is found to shrivel up a little and become nearly as tough as parchment, and when dried to be remarkably inflammable, catching fire at so low a temperature as 356°, and burning without any nitrous odour (Pelouze). Or if the strong undiluted nitric acid of commerce be mixed with an equal weight of oil of vitriol, and cotton-wool be immersed in the mixture for a minute or two and afterwards washed with water, it is converted into gun-cotton, without injury to the cotton fibre (Schönbein).

Nitric acid forms an important class of salts, the nitrates, which occasion deflagration when fused with a combustible at a high temperature, from the oxygen in their acid, and are remarkable as a class for their general solubility, no nitrate being insoluble in water. The nitrate of the black oxide of mercury is perhaps the least soluble of these salts. The nitrates of potassa, soda, ammonia, baryta, and strontia, are anhydrous; but the nitrates of the extensive magnesian class of oxides all contain water in a state of intimate combination, and have a formula analogous to that of hydrated nitric acid, or the nitrate of water itself. Of the four atoms of water contained in hydrated nitric acid of sp. gr. 1.42, one is combined with the acid as base, and may be named *basic* water, while the other three are in combination with the nitrate of water, and may be termed the *constitutional* water of that salt. The same three atoms of constitutional water are found in all the magnesian nitrates, with the addition often of another three atoms of water, as appears from the following formulæ: —

Nitric acid, 1.42	$HO.NO_5+3HO$
Prismatic nitrate of copper	$CuO.NO_5+3HO$
Rhomboidal nitrate of copper	$CuO.NO_5+3HO+3HO$
Nitrate of magnesia	$MgO.NO_5+3HO+3HO$

It is doubtful whether the proportion of constitutional water in any of these nitrates can be reduced below 3 atoms by heat without the loss of a portion of nitric acid at the same time, and the partial decomposition of the salt. The nitrates of the potassa and magnesian classes do not combine together, and no double nitrates are known, nor nitrates with excess of acid. The nitrates with excess of metallic oxide, which are called subnitrates, appear to be formed on the type of the magnesian class: the subnitrate of copper, being $CuO.NO_5 + 3CuO.3HO$ (Gerhardt), or nitrate of copper with 3 atoms hydrated oxide of copper. The water is strongly retained, and requires a temperature of 300° to expel it. The nitrate of red oxide of mercury is $HgO.NO_5 + HgO$ (Kane).

Nitric acid in a solution cannot be detected by precipitating that acid in combination with any base, as the nitrates are all soluble, so that tests of another nature must be had recourse to, to ascertain its presence. A highly diluted solution of sulphate of indigo may be boiled without change, but on adding to it at the boiling temperature a liquid containing free nitric acid, the blue colour of the indigo is soon destroyed. If it is a neutral nitrate which is tested, a little sulphuric acid should be added to the solution, to liberate the nitric acid, before mixing it with the sulphate of indigo. It is also necessary to guard against the presence of a trace of nitric acid in the sulphuric acid. Another test of the presence of nitric acid has been proposed by De Richemont. The liquid containing the nitrate is mixed with rather more than an equal bulk of oil of vitriol, and when the mixture has become cool, a few drops of a strong solution of protosulphate of iron are added to it. Nitric oxide is evolved, and combines with the protosulphate of iron, producing a rose or purple tint even when the quantity of nitric acid is very small. One part of nitric acid in 24,000 of water has been detected in this manner. Free nitric acid also is incapable of dissolving gold-leaf, although heated upon it, but acquires that property when a drop of hydrochloric acid is added to it. But in testing the presence of this acid, it is always advisable to neutralize a portion of the liquor with potassa, and to evaporate so as to obtain the thin prismatic crystals of nitre, which may be recognised by their form, by their cooling nitrous taste, their power to deflagrate combustibles at a red heat, and by the characteristic action of the acid they contain, when liberated by sulphuric acid, upon copper and other metals, in which ruddy nitrous fumes are produced.

[When obtained from nitrate of soda, it may contain iodine. This impure acid yields, on distillation, a sublimate of iodine after all the nitric acid has come over. Neutralized with potassa, mixed with a solution of starch, and sulphuric acid added drop by drop, the liquid assumes a blue colour (Gmelin's Handbook, vol. ii. p. 393). — R. B.]

If nitric acid be rigidly pure, it may be diluted with distilled water, and is not disturbed by nitrate of silver, nor by chloride of barium, the first of which discovers the presence of hydrochloric acid by producing a white precipitate of chloride of silver; the last discovers sulphuric acid by forming the white insoluble sulphate of baryta. The fuming nitric acid may be freed from hydrochloric acid, by retaining it warm on a sand-bath for a day or two, when the chlorine of the hydrochloric acid goes off as gas. To free it from sulphuric, it should be diluted with a little water, and distilled from nitrate of baryta; but the process for nitric acid which has been described gives it without a trace of sulphuric acid, when carefully conducted.

Uses. — Nitric acid is sometimes used in the fumigations required for contagious diseases, particularly in wards of hospitals from which the patients are not removed, the fumes of this acid being greatly less irritating than those of chlorine. For the purpose of fumigation, pounded nitre and concentrated sulphuric acid are used, being heated together in a cup. Nitric acid is par excellence the solvent of metals, and has other most numerous and varied applications not only in chemistry, but likewise in the arts and manufactures.

NITROGEN AND HYDROGEN — AMMONIA.

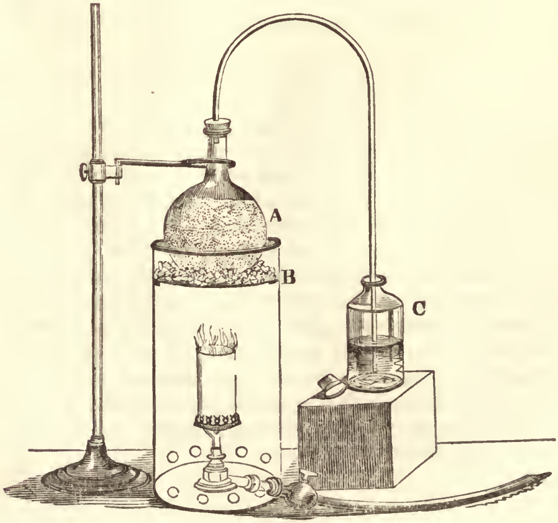
Eq. 17 *or* 212.5; H_3N; *density* 596.7;

With hydrogen, nitrogen forms a remarkable gaseous compound — ammonia, which derives its name from sal ammoniac, a salt from which it is generally extracted, and which again was so named from being first prepared in the district of Ammonia, in Libya. Ammonia is produced in the destructive distillation of all organic matters containing nitrogen, which has given rise to one of its popular names, the Spirits of Hartshorn. It is also produced during the putrefaction of the same matters, and finds its way into the atmosphere (page 252). A trace of it is always found in the native oxides of iron, in the varieties of clay, and in some other minerals.

Nitrogen and hydrogen mixed together do not exhibit any disposition to combine, even when heated; but if electric sparks be taken through a mixture of those gases, particularly with the presence of any acid vapour, a sensible trace of a salt of ammonia is produced. Hydrogen, however, if evolved in contact with nitrogen, will in certain circumstances form ammonia. Thus in the rusting of iron in water containing air or nitrogen and carbonic acid, the hydrogen which is then evolved from the decomposition of the water, appears to combine in its nascent state with nitrogen. If, while zinc is dissolving in dilute sulphuric acid, nitric acid be added drop by drop till the evolution of hydrogen gas ceases, the latter will be found to have united with the nitrogen of the nitric acid, and much ammonia to be formed; the oxygen of the nitric acid combining with hydrogen also, to form water, at the same time. If the proportion of nitric acid be relatively small, Mr. Nesbitt finds that it may be entirely converted into ammonia in this manner. When zinc is dissolved in nitric acid alone, which is neither much diluted nor very strong, but in an intermediate condition, the same suppression of hydrogen and formation of ammonia is observed.

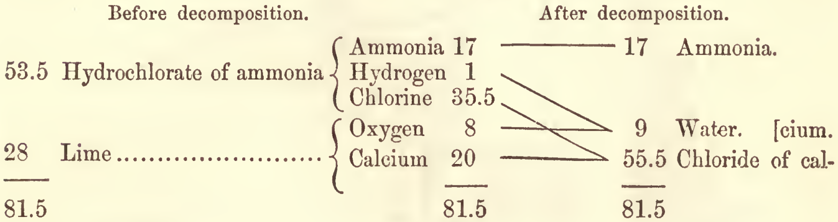
Preparation. — In a state of purity, ammonia is a gas, of which the well-known *liquor* or *aqua ammoniæ* is a solution in water. This solution, which is of constant use as a reagent, is prepared by mixing intimately sal ammoniac (hydrochlorate of ammonia) with an equal weight of slaked lime, introducing the mixture into a glass retort or bolt-head, which is afterwards filled up with slaked lime (A, fig. 118), and

Fig. 118.



distilling by the diffused heat of a chauffer or sand-pot. If recourse is had to the gas-flame, the heat may be conveniently diffused by placing the burner within a cylinder of sheet iron about 14 inches in height, as represented in the figure, with a perforated stage B, covered with small fragments of pumice-stone, on which the flask A is supported. Ammoniacal gas comes off, which should be conducted into a quantity of distilled water in the bottle C, to condense it, equal to the weight of the salt employed. Chloride of calcium and the excess of lime remain in the retort, and a considerable quantity of water is liberated in the process, and distils over with the ammonia. This reaction is explained in the following diagram:—

PROCESS FOR AMMONIA.



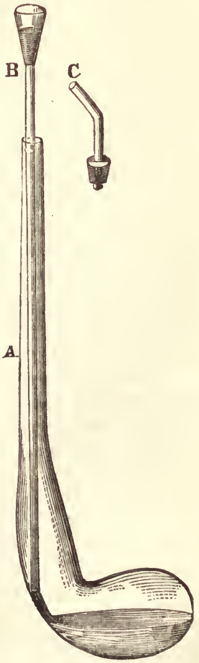
Before decomposition.				After decomposition.	
53.5	Hydrochlorate of ammonia	Ammonia	17	17	Ammonia.
		Hydrogen	1		
		Chlorine	35.5		
28	Lime	Oxygen	8	9	Water.
		Calcium	20	55.5	Chloride of calcium.
81.5			81.5	81.5	

Or in symbols:

$$NH_4Cl \text{ and } CaO = NH_3 \text{ with } HO \text{ and } CaCl.$$

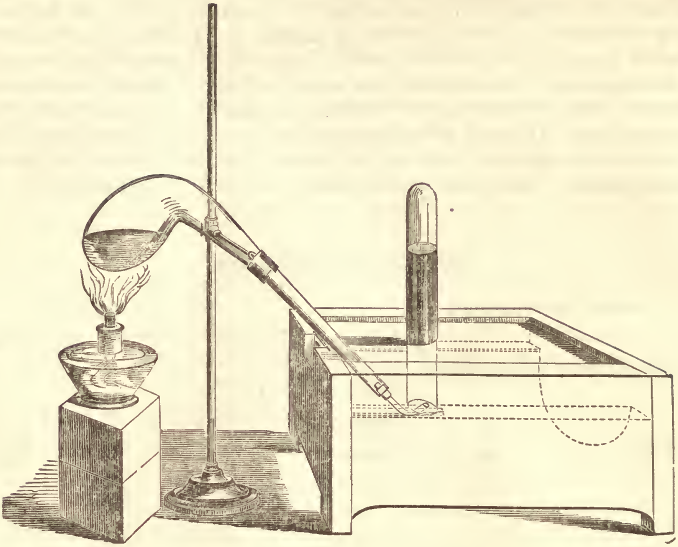
To obtain ammoniacal gas, a portion of the solution prepared by the preceding process may be introduced into a small plain retort, A (fig. 119), by means of the long funnel B; and the short bent tube C being adapted by a perforated cork to the mouth of the retort, the liquid is boiled by a gentle heat, when the gas is first expelled from its superior volatility, and collected in a jar filled with mercury, and inverted over the mercurial trough (fig. 120, page 266). Or the gas may be derived at once from sal ammoniac, mixed with twice its weight of quicklime in a small retort, and collected over mercury.

FIG. 119.



Properties.—Ammonia is a colourless gas, of a strong and pungent odour, familiar in spirits of hartshorn. It is composed of 2 volumes of nitrogen and 6 of hydrogen, condensed into 4 volumes, which form the combining measure of this gas. Ammonia is resolved into its constituent gases, in these proportions, when transmitted through an ignited porcelain tube containing platinum, iron, or copper wire. The two latter metals absorb a little nitrogen (Despretz), and become brittle, but the platinum remains unaltered. By a pressure of 6.5 atmospheres, at 50°, it is condensed into a transparent colourless liquid, of which the sp. gr. is 0.731 at 60°. Ammoniacal gas is inflammable in air in a low degree, burning in contact with the flame of a taper. A small jet of this gas will also burn in oxygen. A mixture of ammoniacal gas with an equal volume of nitrous oxide may be detonated by the electric spark, and affords water and nitrogen. Water is capable of dissolving about 500 times its volume of ammoniacal gas in the cold, and the solution is always specifically lighter, and has a lower boiling point than pure water. According to the observations of Davy, solutions of sp. gr. 0.872, 0.9054, and 0.9692, contain respectively 32.5, 25.37,

FIG. 120.



and 9.5 per cent. of ammonia. Mr. Griffin, who has constructed a table of the densities of solutions of ammonia from experiment, finds that no sensible condensation of volume occurs in these mixtures, and that their densities are the mean of those of water 1 and anhydrous liquid ammonia, supposing the latter to be 0.7083 at 62° (Mem. Chem. Soc. iii. 189). Ammoniacal gas is also largely soluble in alcohol.

Solution of ammonia has an acrid alkaline taste, and produces blisters on the tongue and skin. When cooled slowly to —40°, it crystallizes in long needles of a silky lustre. The solution has a temporary action upon turmeric paper, which it causes to be brown while humid; it also restores the blue colour of litmus reddened by an acid, changes the blue colour of the infusion of red cabbage into green, and neutralizes the strongest acids, properties which it possesses in common with the fixed alkalies. It is distinguished as the volatile alkali. When ammonia is free, it may always be discovered, by its odour, by forming dense white fumes with hydrochloric acid, and by producing a deep blue solution with salts of copper.

Ammonia, in solution, is decomposed by chlorine, with the evolution of nitrogen gas and formation of hydrochlorate of ammonia: when ammonia and chlorine, both in the state of gas, are mixed together, the action that ensues is attended with flame. Dry iodine absorbs ammoniacal gas, and forms a brown viscous liquid, which water decomposes, dissolving out hydriodate of ammonia, and leaving a black powder, which is the explosive iodide of nitrogen.

Ammonia forms several classes of compounds with acids and salts (page 166), and exhibits highly curious reactions with many other substances, which do not admit of being discussed so early, but which I shall return to later in the work. [*See Supplement*, p. 766.]

SECTION IV.

CARBON.

Eq. 6 *or* 75; C; *density of vapour* (*hypothetical*) 416

Carbon is found in great abundance in the mineral kingdom united with other substances, as in coal, of which it is the basis, and in the acid of carbonates: it is also the most considerable element of the solid parts of both animals and vegetables.

It exists in nature, or may be obtained by art, under a variety of appearances, and possessed of very different physical properties. Carbon is a dimorphous body, occurring crystallized in the diamond and graphite in wholly different forms, and when artificially produced forming several amorphous varieties of charcoal which are very unlike each other. [*See Supplement*, p. 769.]

Diamond.—This valuable gem is found throughout the range of the Ghauts in India, but chiefly at Golconda, in Borneo, and also in Brazil. It is always associated with transported materials, such as rolled gravel, or found in a sort of breccia or pudding-stone, composed of fragments of jasper, quartz, and calcedony, so that it is still a question whether the diamond is of mineral or vegetable origin. On removing the crust with which the crystals are covered, they are exceedingly brilliant, refract light powerfully, and are generally perfectly transparent, although diamonds are sometimes black, blue, and of a beautiful rose-colour. The primitive form of diamond is the regular octohedron, or two four-sided pyramids, of which the faces are equilateral triangles, applied base to base (fig. 55, page 143). It is more frequently found in the pyramidal octohedron,—a figure bounded by 24 sides, which presents the general aspect of a regular octohedron, on every facet of which has been placed a low pyramid of three facets; or, each facet of the octohedron is replaced by 6 secondary triangles, and the crystal becomes almost spherical, and presents 48 facets. These facets often appear curved from the effect of attrition. The diamond can always be cleaved in the direction of the faces of the octohedron, which possess that particular brilliancy characteristic of the diamond. It is the hardest of the gems. An edge of its crystal formed by flat planes only scratches glass, but if the edge is formed of curved faces, like the edge of a convex lens, it then, besides abrading the surface, produces a fissure to a small depth, and in the form of the glazier's diamond is used to cut glass. The weight of diamonds is generally estimated by the *carat*, which is about 3.2 grains. The diamond is remarkably indestructible, and may be heated to whiteness in a covered crucible without injury, but it begins to burn in the open air, at about the melting point of silver, charcoal sometimes appearing on its surface, and is entirely converted into carbonic acid gas. When heated to the highest degree between the charcoal points of a strong voltaic battery, the diamond swells up considerably, and divides into portions. After cooling, it is found entirely altered in appearance, having become of a metallic gray, friable, and resembling in every respect the coke from bituminous coal. This experiment appears to show that a high temperature is unfavourable to the existence of diamonds, and that they cannot therefore be originally formed at a very elevated temperature. The diamond is quickly consumed in fused nitre, when the carbonic acid is retained by the potash; this is a simple mode of analyzing the diamond, by which it has been proved to be pure carbon. The diamond is a non-conductor of electricity. Its density varies from 3.5 to 3.55.

Graphite.—This mineral, which is also known as Black Lead and Plumbago, occurs in rounded masses deposited in beds in the primitive formations, particularly in granite, mica-schist, and primitive limestone. Borrowdale in Cumberland is a celebrated locality of graphite, and affords the only specimens which are sufficiently hard for making pencils. It is occasionally found crystallized in plates which are six-sided tables. Graphite may also be produced artificially, by putting an excess of charcoal in contact with fused cast iron, when a portion of the carbon dissolves, and separates again on cooling, in the form of large and beautiful leaflets. In the condition of graphite, carbon is perfectly opaque, soft to the touch, possessed of the metallic lustre, and of a specific gravity from 1.9 to 2.3. It always contains iron and manganese, apparently in the state of oxides, and in combination with silicic and titanic acids, sometimes to the extent of 28 per cent., but in some specimens, as in those from Barreros in Brazil, not more than a trace of those metals is found, which is to be considered an accidental constituent, and not essential to the mineral. Neither in the form of diamond nor graphite does carbon exhibit any indication of fusion or volatility under the most intense heat. *Anthracite* is often nearly pure carbon, but always contains a portion of hydrogen, and is related to bituminous coal, and not to graphite. [*See Supplement*, p. 770.]

Charcoal.—Owing to its infusibility carbon presents itself under a variety of aspects, according to the structure of the substance from which it is derived, and the accidental circumstances of its preparation. The following are the principal varieties: gas carbon, lamp-black, wood charcoal, coke, and ivory black.

1. Gas carbon has the metallic lustre, and a density of 1.76; it is compact, generally of a mammillated structure, but sometimes in fine fibres, and considerably resembles graphite, but is too hard to give a streak upon paper. It is the product of a slow deposition of carbon from coal gas at a high temperature, and is frequently found to line the gas retorts to a considerable thickness, and to fill up accidental fissures in them (Dr. Colquhoun, Ann. of Philos., New Ser., vol. xii. p. 1).

2. Lamp-black is the soot of imperfectly burned combustibles, such as tar or resin. Carbon is deposited in a powder of the same nature, and of the purest form, when alcohol vapour or a volatile oil is transmitted through a porcelain tube at a red heat; and the lustrous charcoal, which is obtained on calcining, in close vessels, starch, sugar, and many other organic substances, which fuse and afford a bright vesicular carbon of a metallic lustre, is possessed of the same characters. The charcoal of the latter sources, however, always retains traces of oxygen and hydrogen. Lamp-black is deficient in an attraction for organic matters in solution, which ordinary charcoal possesses.

3. Wood charcoal. Wood was found by Karsten to lose 57 per cent. of its weight when thoroughly dried at 212°, and 10 per cent. more at 304°. The remaining 33 parts of baked wood afforded, when calcined, 25 of charcoal, while 100 parts of the same wood calcined, without being previously dried, left only 14 per cent. of carbon. It is the absence of this large quantity of water which causes the heat of burning charcoal to be so much more intense than that of wood. When calcined at a high temperature, charcoal becomes dense, hard, and less inflammable. The knots in wood sometimes afford a charcoal which is particularly hard, and is used in polishing metals, but it contains silica. From the minuteness of its pores, the charcoal of wood absorbs many times its volume of the more liquefiable gases; such as ammoniacal gas, hydrochloric acid, hydrosulphuric acid, and carbonic acid, condensing 90 times its volume of the first, and 35 of the last: of oxygen, it condenses 9.25 volumes; of nitrogen, 7.5 volumes; and of hydrogen, 1.75 volumes. It also absorbs moisture with avidity from the atmosphere, and other condensible vapours, such as odoriferous effluvia. From this last property freshly calcined charcoal, when wrapt up in clothes which have contracted a disagreeable odour, destroys it, and has a considerable effect in retarding the putrefaction of organic matter with which it is placed in contact. Water is also found to remain sweet, and wine to be improved in quality, if kept in casks of which the inside has been charred. In the state of a coarse powder, wood charcoal is particularly applicable as a filter for spirits, which it deprives of the essential oil which they contain. It is much less destructible by atmospheric agencies than wood, and hence the points of stakes are often charred, before being driven into the ground, in order to preserve them. Charcoal decomposes the vapour of water at a red heat, giving rise to a gaseous mixture, which was found by Bunsen to consist, in 100 volumes, of hydrogen 56, carbonic oxide 29, carbonic acid 14.8, and light carburetted hydrogen 0.2 volume.

4. The coke of those species of coal which do not fuse when heated is a remarkably dense charcoal, considerably resembling that of wood, and of great value as fuel, from the high temperature which can be produced by its combustion. When burned it generally leaves 2 or 3 per cent. of earthy ashes, while the ashes from wood charcoal seldom exceed 1 per cent. The density of pulverised coke varies from 1.6 to 2.0. Coke and wood charcoal, after being strongly heated, are good conductors of electricity.

5. Ivory black, Bone black, and Animal charcoal, are names applied to bones calcined or converted into charcoal in a close vessel. The charcoal thus produced

is mixed with not less than 10 times its weight of phosphate of lime, and being in a state of extreme division, exposes a great deal of surface. It possesses a remarkable attraction for organic colouring matters, and is extensively used in withdrawing the colouring matter from syrup in the refining of sugar, from the solution of tartaric acid, and in the purification of many other organic liquids. The usual practice, which was introduced by Dumont, is to filter the liquid hot through a bed of this charcoal in grains of the size of those of gunpowder, and of two or three feet in thickness. It is found that the discolouring power is greatly reduced by dissolving out the phosphate of lime from ivory black by an acid, although this must be done in certain applications of it, as when it is used to discolour the vegetable acids. A charcoal possessed of the same valuable property even in a higher degree for its weight, is produced by calcining dried blood, horns, hoofs, clippings of hides, in contact with carbonate of potash, and washing the calcined mass afterwards with water. Even vegetable matters afford a charcoal possessed of considerable discolouring power, if mixed with chalk, calcined flint, or any other earthy powder, before being carbonized. One hundred parts of pipe clay made into a thin paste with water, and well mixed with 20 parts of tar and 500 of coal finely pulverized, have been found to afford, after the mass was dried and ignited out of contact with air, a charcoal which was little inferior to bone black in quality. When charcoal which has been once used in such a filter is calcined again, it is found to have lost much of its discolouring power. This is owing to the deposition upon its surface of a lustrous charcoal, of the lamp-black variety, produced by the decomposition of the organic colouring matters, which has little or no discolouring power. But if the charcoal of the sugar filters be allowed to ferment, the foreign matter in it is destroyed; and if afterwards well washed with water and dried, before being calcined, it will be found to recover a considerable portion of its original power.

Bussy has constructed, from observation, the following table of the efficiency of the different charcoals. (Journ. de Pharm. t. viii. p. 257). These substances are compared with ivory black, as being the most feeble species, although this is superior by several degrees to the best wood charcoal. The relative efficiency, it will be observed, is not the same for two different kinds of colouring matter:—

Species of charcoal same weight.	Relative decolouration of sulphate of indigo.	Relative Decolouration of Syrup.
Blood charred with carbonate of potassa	50	20
Blood charred with chalk	18	11
Blood charred with phosphate of lime	12	10
Glue charred with carbonate of potassa	36	15.5
White of egg charred with the same	34	15.5
Gluten charred with the same	10.6	8.8
Charcoal from acetate of potassa	5.6	4.4
Charcoal from acetate of soda	12	8.8
Lamp-black, not calcined	4	3.3
Lamp-black calcined with carbonate of potassa	15.2	10.6
Bone charcoal, after the extraction of the earth of bones by an acid, and calcination with potassa	45	20
Bone charcoal treated with an acid	1.87	1.6
Oil charred with the phosphate of lime	2	1.9
Bone charcoal, in its ordinary state	1	1

This remarkable action of charcoal in withdrawing matters from solution is certainly an attraction of surface, but it is capable, notwithstanding, of overcoming chemical affinities of some intensity. The matters remain attached to the surface of the charcoal, without being decomposed or altered in nature. For if the blue sulphate of indigo be neutralized and then filtered through charcoal, the whole colouring matter is retained by the latter, and the filtered liquid is colourless. But a solution of caustic alkali will divest the charcoal of the blue colouring matter, and carry it away in solution. The salts of quinine, morphine, and other organic bases and bitter principles, are carried down by animal charcoal used in excess (Warington, Mem. Chem. Soc. iii. 326). Hence this substance is a very general antidote to vegetable poisons, as was proved by Dr. Garrod. Other substances also are carried down by animal charcoal, besides organic matters. Lime from lime water, iodine from solution in iodide of potassium, hydrosulphuric acid from solution in water, soluble subsalts of lead, and metallic oxides dissolved in ammonia or caustic potassa; but it has little or no action upon most neutral salts. The charcoal is apt with time to react upon the substance it carries down, probably from their closeness of contact, reducing the oxides of silver, lead, and copper, for instance, to the metallic state in a short time. Animal charcoal soon disappears when heated in chlorine water, and is converted into carbonic acid; and the affinities of carbon generally are more active in this than in its other forms. [*See Supplement*, p. 769.]

Carbon is chemically the same under all these forms. This element cannot be crystallized artificially by the usual methods of fusion, solution or sublimation, if we except its solution, in cast iron, which gives it in the form of graphite and not of the diamond. It is chemically indifferent to most bodies at a low temperature, but combines directly with some metals by fusion, and forms compounds named *carburets* or *carbides:* in these compounds, however, the metal is most probably the negative constituent. When heated to low redness it burns readily in air or oxygen, forming a gaseous compound carbonic acid, which, when cool, has sensibly the same volume as the original oxygen. With half the proportion of oxygen in carbonic acid, carbon forms a protoxide, carbonic oxide gas. The last gas being supposed similar to steam or to nitrous oxide in its constitution, will be composed of 2 volumes of carbon vapour and 1 volume of oxygen gas condensed into 2 volumes, an assumption upon which the density of carbon vapour, which there are no means of determining experimentally, is usually calculated, and made about 420; the combining measure of this vapour containing 2 volumes (page 129). The density deduced from the equivalent of carbon is more nearly 416.[1] That the equivalent of carbon is exactly 6, as originally maintained by Dr. Prout, has been established beyond doubt by M. Dumas, by the combustion of the diamond in a stream of oxygen gas. Pure carbon then unites with oxygen in the proportion of 3 to 8 exactly, or 6 to 16, to form carbonic acid (p. 272).

Uses.—Several valuable applications of this substance have already been incidentally described. Carbon may be said to surpass all other bodies whatever in its affinity for oxygen at a high temperature; and being infusible, easily got rid of by combustion, and forming compounds with oxygen which escape as gas, this body is more suitable than any other substance to effect the reduction of metallic oxides; that is, to deprive them of their oxygen, and to produce from them the metal with the properties which characterize it.

CARBONIC ACID.

Eq. 22 or 275; CO_2; *density* 1529.0; ☐☐

This gas was first discovered to exist in lime-stone and the mild alkalies, and to be expelled from the first by heat, and from both by the action of acids, by Dr. Black, and was named by him Fixed Air. He also remarked that the same gas is formed in respiration, fermentation, and combustion; it was afterwards proved to contain carbon by Lavoisier.

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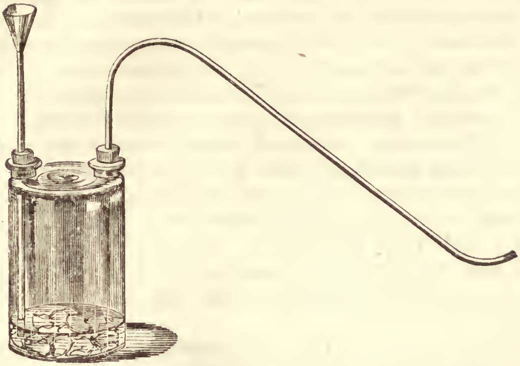
[1] The number for carbon vapour deduced from the density of oxygen gas, that is, six-sixteenths of that density, is 414.61 (page 130); while six-fourteenths of the density of nitrogen is 416.304, and six times the density of hydrogen, 415.56. The density of nitrogen is probably the least objectionable, and the number deduced from it for carbon (416) therefore the safest.

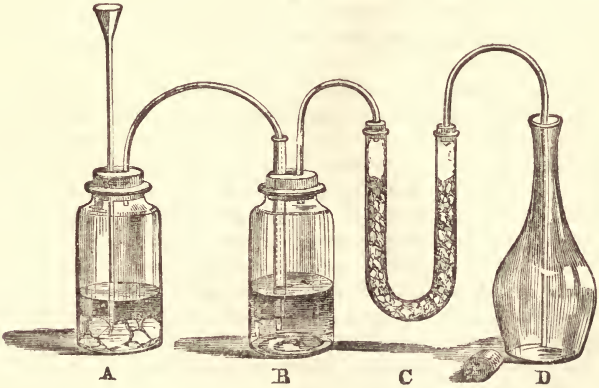
FIG. 121.



Preparation.—Carbonic acid is readily procured by pouring hydrochloric acid of sp. gr. 1.1, upon fragments of marble contained in a gas-bottle (fig. 121), or by the action of diluted sulphuric acid upon chalk. A gas comes off with effervescence, which may be collected at the water trough, but cannot be retained long over water without considerable loss, owing to its solubility.

From the great weight of carbonic acid a bottle may be filled with this gas by displacing air. The gas being evolved in the gas-bottle A (fig. 122), is first conveyed into a wash-bottle B, containing water, to condense any hydrochloric acid vapour with which the gas may be accompanied; then passing through a U-shaped drying tube C, containing fragments of chloride of calcium, to absorb aqueous vapour, and then conveyed to the lower part of the bottle D. When generated in the close apparatus of Thilorier for the purpose of liquefying it (page 77), this gas is evolved from bicarbonate of soda and sulphuric acid.

FIG. 122.



Properties.—This gas extinguishes flame, does not support animal life, and renders lime water turbid. Its density is considerable, being 1529 (Regnault), or a half more than that of air, the gas containing 2 volumes of the hypothetical carbon vapour and 2 volumes of oxygen, condensed into 2 volumes, which form the combining measure. Cold water dissolves rather more than an equal volume of this gas; the solution has an agreeable acidulous taste, and sparkles when poured from one vessel into another. It communicates a wine-red tint to litmus paper, which disappears again when the paper dries; when poured into lime water, it first throws down a white flaky precipitate of carbonate of lime or chalk, which it afterwards redissolves if the solution of the gas be added in excess. The quantity of this gas which water takes up is found to be sensibly proportional to the pressure; a very large volume of the gas is forced into soda, magnesia, and other aërated waters, much of which escapes on removing the pressure from these liquids.

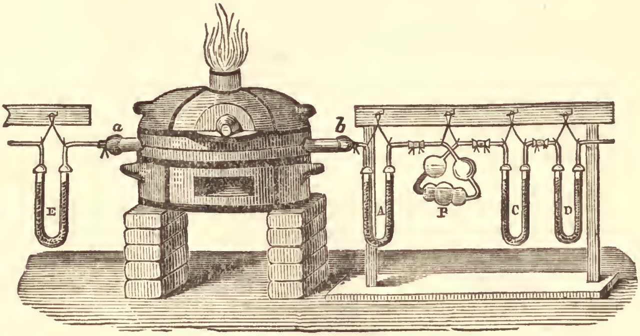
Liquefied by pressure, carbonic acid has an elastic force of 38·5 atmospheres at 32° (Faraday). The specific gravity of liquid carbonic acid, at the same temperature, is 0·83: it dilates remarkably from heat, its expansion being four times greater than that of air, 20 volumes of the liquid at 32° becoming 29 at 86°, and its density varying from 0.9 to 0.6 as its temperature rises from —4° to 86°. (Thilorier, Annal. de Chim. et de Phys. lx. p. 427). It is a colourless liquid, which mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and bisulphide of carbon, but is insoluble in water and fat oils. At temperatures below —72° it is solid (page 80).

Potassium heated in a small glass bulb blown upon a tube, through which gaseous carbonic acid is transmitted, undergoes oxidation, and liberates carbon, the existence of which in the gas may thus be shown; or, for this experiment, a cleansed and dry Florence oil-flask may be filled, by displacement, with the dried gas (fig. 122), and a pellet of potassium being introduced, combustion may be determined by applying the flame of an Argand spirit-lamp for a few seconds to the bottom of the flask. But burning phosphorus, sulphur, and other combustibles, are immediately extinguished by carbonic acid, and the combustion does not cease from the absence of oxygen only, but from a positive influence in checking combustion which this gas exerts, for a lighted candle is extinguished in air containing no more than one-fourth of its volume of carbonic acid. It is generally believed that any mixture of carbonic acid and air will support the respiration of man, which will maintain the flame of a candle, and therefore a lighted candle is often let down into wells or pits suspected to contain this gas, to ascertain whether they are safe or not. But although air in which a candle can burn may not occasion immediate insensibility, still the continued respiration for several hours of air containing not more than 1 or 2 per cent. of carbonic acid, has been found to produce alarming effects (Broughton). The accidents from burning a pan of charcoal in close rooms are occasioned by this gas. It acts as a narcotic poison upon the system. A small animal thrown into convulsions from the respiration of this gas, may be recovered by sudden immersion in cold water.

Carbonic acid is thrown off from the lungs in respiration, as may be proved by directing a few expirations through lime-water. The air of an ordinary expiration contains, on an average, as observed by Dr. Prout, 3·45 per cent. of its volume of this gas, and the proportion varies from 3.3 to 4.1 per cent.,—being greatest at noon, and least during the night. Carbonic acid is also a product of the vinous fermentation, and is the cause of the agreeable pungency of beer, ale, and other fermented liquors, which become stale when exposed to the air from the loss of this gas. It also exists in all kinds of well and spring water, and contributes to their pleasant flavour, for water which has been deprived of its gases by boiling is insipid and disagreeable. Carbonic acid is also largely produced by the combustion of carbonaceous fuel, and appears to exist in considerable quantity in the earth, being discharged by active volcanoes, and from fissures in their neighbourhood, long after the volcanoes are extinct. The Grotto del Cane in Italy owes its mysterious properties to this gas, and many mineral springs, such as those of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. It comes thus to be always present in the atmosphere in a sensible, although by no means considerable proportion (page 251).

Composition of carbonic acid.—The composition of this substance, which, like that of water, is one of the fundamental data of chemical analysis, is determined with extreme exactness in the following manner:—A known weight of a very pure form of carbon, such as the diamond, is placed in a little trough or cradle of plati num, which is introduced into a porcelain tube *a b* (fig.123), placed across a furnace. To effect the combustion of the carbon, the end *a* of this tube is made to communicate by means of a glass tube with an apparatus supplying a stream of oxygen gas, perfectly dried by passing through the U tube E, which contains fragments of pumice impregnated with concentrated sulphuric acid. The second and fourth U tubes, A and D, are charged in the same manner. The bulb apparatus B contains a concentrated solution of caustic potassa, and the pumice in the adjoining U tube C is impregnated with the same fluid. These tubes, B and C, containing the alkali, with the tube following them, D, are accurately weighed together in a good balance.

FIG. 123.



The different parts being connected by short tubes of caoutchouc, as represented in the figure, the apparatus is then filled with oxygen gas, which ought to be slowly disengaged. The tube *a b*, which contains the carbon, is heated to redness, and the latter soon enters into combustion, and is changed into carbonic acid. The gases pass through the series of tubes, A, B, C, D. In A, any trace of moisture is absorbed by the sulphuric acid, which may escape from the inner surface of the tube *a b* when heated, and in B and C the carbonic acid produced is absorbed by the caustic alkali. The excess of oxygen, which passes on uncondensed, takes up a little aqueous vapour in B and C, which tends to diminish the weight of the potassa apparatus; for, although the tension of the vapour of the alkaline solution is small, the latter cannot be used so concentrated as to make the tension insensible. The last U tube D remedies this inconvenience by drying the gases perfectly again before they escape into the atmosphere.

In such a combustion the formation of a little carbonic oxide gas is to be apprehended. This is provided against by filling the part of the tube *a b*, next *b*, with very porous oxide of copper, which is heated to redness during the experiment. In passing through this oxide, any small quantity of carbonic oxide which may exist is necessarily converted into carbonic acid. The oxide of copper is separated by a pad of asbestos from that part of the tube containing the little cradle with the carbon. The evolution of the oxygen is also continued for some time after the combustion of the carbon is complete, in order to sweep the tubes by means of that gas, and carry forward the whole carbonic acid formed into the potassa bulbs where it is absorbed.

On disconnecting the apparatus afterwards, and examining the cradle in which the carbon was placed, to ascertain whether its combustion is complete, a little incombustible earthy matter, not exceeding a few hundredths of a grain, will generally be found remaining, which had existed mechanically diffused through the carbon. The weight of the cradle and residue, deducted from the original weight of the cradle and carbon, gives obviously the exact weight of the carbon consumed; while the original weight of the system of tubes B, C, and D, deducted from their final weight, gives the exact weight of carbonic acid formed. (Cours Elémentaire de Chimie, par M. V. Regnault).

It is found in this way that 6 parts of carbon produce exactly 22 parts of carbonic acid, or carbonic acid contains—

1 eq. carbon	6	27.27
2 eq. oxygen	16	72.73
	22	100.00

Carbonates.—Carbonic acid combines with bases, and forms the class of carbonates. The hydrate of this acid seems incapable of existing in an uncombined state, but it exists in the alkaline bicarbonates, which are double carbonates of water and the alkali. If this hydrate were formed, we may presume that it would be analogous to the crystallized carbonate of magnesia, of which the formula is $MgO,CO_2+HO+2HO$, and also the same with another $2HO$; the salt of magnesia of most acids resembling the salt of water. Carbonate of lime, in the hydrated condition, has a similar formula. Carbonates of potassa, soda, and ammonia, retain a strong alkaline reaction, owing to the weakness of this acid, and the carbonates generally are decomposed with effervescence by all other acids, except the hydrocyanic.

Uses.—Carbonic acid is used in the preparation of aërated waters. The strong vessels in which the impregnation is effected, should be of copper, well tinned, and not of iron, as with the concurrence of water carbonic acid acts strongly upon that metal. It is sometimes desirable to remove carbonic acid from air or other gaseous mixtures, and this is generally done by means of caustic alkali or lime-water. When very dry, or so humid as to be actually wet, the hydrate of lime absorbs this gas with much less avidity than when of a certain degree of dryness, in which it is not so dry as to be dusty, but at the same time not sensibly damp. The dry hydrate may be brought at once to this condition, by mixing it intimately with an equal weight of crystallized sulphate of soda in fine powder; and this mixture, in a stratum of not more than an inch in thickness, intercepts carbonic acid most completely, and may rise in temperature to above 200°, from the rapid absorption of the gas. It is quite possible to respire through a cushion of that thickness, filled with the mixture, and such an article might be found useful by parties entering an atmosphere overcharged with carbonic acid, like that of a coal-mine after the occurrence of an explosion of fire-damp.

Carbonic acid is the highest degree of oxidation of which carbon is susceptible; but another oxide of carbon exists containing less oxygen. [*See Supplement*, p. 771.]

CARBONIC OXIDE.

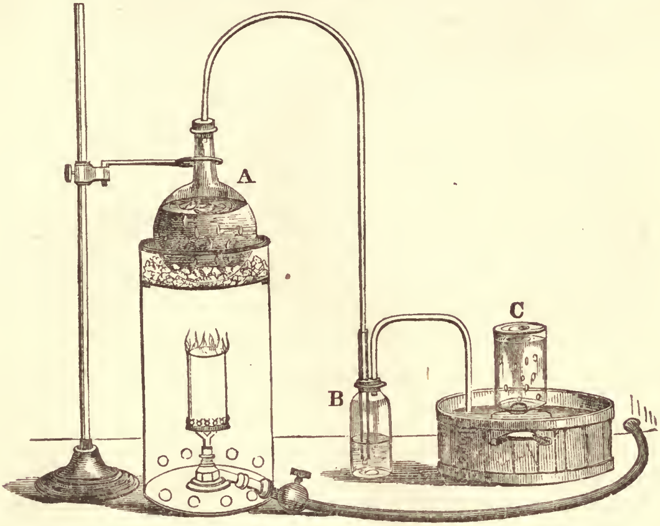
Eq. 14 *or* 175; CO; *density* 967·8; ☐☐

Priestley is the discoverer of this gas, but its true nature was first pointed out by Cruikshanks, and about the same time by Clement and Desormes.

Preparation.—Carbonic acid is readily deprived of half its oxygen, at a red heat, by a variety of substances, and so reduced to the state of carbonic oxide. The latter gas may therefore be obtained by transmitting carbonic acid over red-hot fragments of charcoal contained in an iron or porcelain tube; or by calcining chalk mixed with 1-4th of its weight of charcoal in an iron retort. It is likewise prepared by gently heating crystallized oxalic acid with five or six times its weight of strong oil of vitriol in a glass retort. The latter process affords a mixture of equal volumes of carbonic acid and carbonic oxide, the elements of oxalic acid being carbon and oxygen in the proportion to form these gases, and this acid being incapable of existing except in combination with water or some other base. Now the sulphuric acid unites with the water of the crystallized oxalic acid, and the latter acid being set free is instantly decomposed. The gas of all these processes contains much carbonic acid, of which it may be deprived by washing it with milk of lime, or a strong solution of potassa.

Another process suggested by Mr. Fownes affords a perfectly pure gas. It consists in heating the crystallized ferrocyanide of potassium in a glass retort or flask A (fig. 124), with four or five times its weight of oil of vitriol. The gas may be passed through a wash-bottle B, containing a little water, and be collected in the bottle C over the water-trough in the usual manner. One equivalent of ferrocyanide of potassium and 9 equivalents of water are then resolved into 6 equivalents of carbonic oxide, 2 equivalents of potassa, 1 equivalent of protoxide of iron, and 3 equivalents of ammonia:—

Fig. 124.



$$2K.FeC_6N_3+9HO=6CO+2KO+FeO+3H_3N.$$

Half an ounce of the salt yields 300 cubic inches of carbonic oxide.

*Properties.**—This gas, as has already been stated, is presumed to contain 2 volumes of carbon vapour, and 1 volume of oxygen, condensed into 2 volumes, so that its combining measure is 2 volumes: its density is 967.79 (Wrede). Carbonic oxide is 14 times heavier than hydrogen, like nitrogen, and coincides remarkably in its rate of transpiration (page 86) and other physical properties with the latter gas. It is very fatal to animals, and when inspired in a pure state almost immediately produces coma. Carbonic oxide is not more soluble in water than atmospheric air, and has never been liquefied. It is easily kindled, and burns with a pale blue flame, like that of sulphur, combining with half its volume of oxygen, and forming carbonic acid, which retains the original volume of the carbonic oxide. This combustion is often witnessed in a coke or charcoal fire. The carbonic acid, produced in the lower part of the fire, is converted into carbonic oxide, as it passes up through the red-hot embers, and afterwards burns above them with a blue flame, where it meets with air.

Carbonic oxide is a neutral body, like water, and combines directly with only a very few substances. It unites with an equal volume of chlorine under the influence of the sun's rays, and forms *phosgene* gas or Chloroxicarbonic Gas. As the gases contract to half their volume on combining, the density of this gas is the sum of

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* [*See Supplement*, pp. 771, 772.]

carbonic oxide 968, and chlorine 2440, or 3408; its formula is CO.Cl. Chloroxicarbonic gas is colourless, and has a peculiar suffocating odour. In contact with water it is decomposed at the same time with an equivalent of water; hydrochloric and carbonic acids are produced — that is —

$$CO.Cl \text{ and } HO = CO_2 \text{ and } HCl.$$

Carbonic oxide is also absorbed by potassium gently heated, and that metal is employed to separate this gas from a mixture of hydrogen and gaseous carbohydrogens, as in the analysis of coal gas. But carbonic oxide has been supposed to exist in a greater number of compounds, and to be the radical of a series, of which the following substances are members: —

CARBONIC OXIDE SERIES.

Carbonic oxide	CO
Carbonic acid	$CO+O$
Chloroxicarbonic gas	$CO+Cl$
Oxalic acid	$2CO+O$
Oxamide	$2CO+NH_2$
Carbonoxide of potassium	$7CO+3K$
Rhodizonic acid	$7CO+3HO$
Croconic acid	$5CO+H$
Mellitic acid	$4CO+H$

In these compounds carbonic oxide is represented as playing the part of a simple substance, and forming a variety of products by uniting with oxygen, chlorine, hydrogen, and other elements.

Mellitic, croconic, and rhodizonic acids are sometimes enumerated as oxides of carbon, along with carbonic acid, carbonic oxide, and oxalic acid, but the former bodies have not an equal claim to the same early consideration as the latter compounds.

OXALIC ACID.

Eq. 36 *or* 450; C_2O_3. *Oxalate of water*, HO,C_2O_3+2HO.

This acid, discovered by Scheele in 1776, exists in the form of an acid salt of potassa, in a great number of plants, particularly in the species of *Oxalis* and *Rumex:* combined with lime it also forms a part of several lichens. Oxalate of lime occurs likewise as a mineral, *humboldite*, and forms the basis of a species of urinary calculus. This acid is also produced by the oxidation of carbon in combination, in a variety of circumstances, being the general product of the oxidation of organic substances by nitric acid, hypermanganate of potassa, and by fused potassa. Those matters which contain oxygen and hydrogen in the proportion of water furnish the largest quantity of oxalic acid.

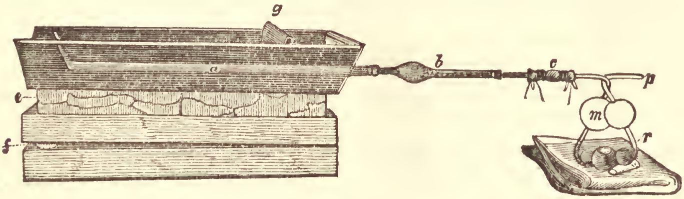
This acid has been derived in quantity from lichens, but it is usually prepared by acting upon 1 part of sugar by 5 parts of nitric acid, of 1.42, diluted with 10 parts of water at a gentle heat till no gas is evolved, and evaporating to crystallize. The crystals must be drained, and crystallized a second time, as they are apt to retain a portion of nitric acid. Acting upon 1 part of sugar, with 6.6 parts of nitric acid, of density 1.245, Mr. L. Thompson obtained 1.1 parts of crystallized oxalic acid. One half of the carbon of the sugar appeared to be converted into oxalic acid, and the other half into carbonic acid; the nitric acid being entirely converted into binoxide of nitrogen, by loss of oxygen.

Oxalic acid forms long, four-sided, oblique prisms, with dihedral summits, or terminated by a single face. These crystals contain three equivalents of water, one of which is basic, and the other two constitutional, or water of crystallization. The latter two may be expelled at a temperature above 212°, and the protohydrate rises at the same time in vapour, and condenses as a woolly sublimate. Heated in a retort, the hydrated acid undergoes decomposition about 311°, and is converted into carbonic oxide, carbonic acid, and formic acid, without leaving any fixed residue. Concentrated nitric acid, with heat, converts oxalic acid into water and carbonic acid. When heated with sulphuric acid, oxalic acid yields equal volumes of carbonic oxide and carbonic acid; C_2O_3 being equivalent to $CO+CO_2$ (page 274). No charring, nor evolution of any other gas, occurs, so that the action of concentrated sulphuric acid affords the means of recognising oxalic acid or any oxalate. Crystallized oxalic acid is soluble in 8 parts of water, at 59°, in its own weight of boiling water, and in 4 parts of alcohol, at 59°.

Oxalic acid is a powerful acid, which combines with bases, and forms a well-defined class of salts,—the oxalates: it disengages carbonic acid easily from all its combinations. Added to lime-water, or any soluble salt of lime, oxalic acid forms a white precipitate—the oxalate of lime, which is a highly insoluble salt. Absolute oxalic acid, C_2O_3, has not been isolated, and appears incapable of existing except in combination with water, or some other base.

Composition of oxalic acid.—The analysis of oxalic acid is effected in the following manner:—Ten grains of the crystals, reduced to powder, are exactly weighed and mixed with 200 or 300 grains of oxide of copper, recently calcined, and perfectly dry. This mixture is introduced into a tube of white Bohemian glass, which is not easily fused, open at one end, about 0.4 inch in internal diameter, and 14 or 15 inches long, the other end being drawn out, bent upward, and sealed (*a*, fig. 125).

Fig. 125.



This is placed in a furnace, of a trough form, as represented in the figure, constructed of sheet iron, and heated to low redness by burning charcoal. Immediately connected with the combustion tube, by means of a perforated cork, is a tube of the form *b*, containing fragments of strongly dried chloride of calcium. In this tube the water of the oxalic acid is condensed, and the weight of that constituent is ascertained by weighing the tube, before and after the combustion. Beyond the chloride of calcium tube, and connected with it by a short caoutchouc tube, *c*, is a glass instrument, *p m r*, containing a strong solution of caustic potassa, of density 1.25 to 1.27, for the absorption of the carbonic acid produced by the combustion of the carbon of the oxalic acid by the oxygen of the oxide of copper. This instrument consists of five balls, of which *m* is larger than the others; no more of the potassa ley is put into it than fills the three central balls, leaving a bubble of air in each. One corner is elevated a little by a cork placed under it, and the whole supported on a folded towel: the potassa balls, when filled with ley, commonly weigh from 760 to 900 grains. This apparatus is also weighed before and after the combustion, and the increase ascertained.

The experiment, when properly conducted, gives 4.29 grains water condensed in the chloride of calcium tube, and 6.98 grains of carbonic acid absorbed in the potassa bulbs. But 4.29 grains of water contain 0.47 grain of hydrogen, and 6.98 grains of carbonic acid contain 1.905 grains of carbon. Now, as oxalic acid contains nothing but carbon, hydrogen, and oxygen, we obtain thus, for the composition of 10 grains of oxalic acid:—

Hydrogen	0.476
Carbon	1.905
Oxygen	7.619
	10.000

To learn the relation between the number of equivalents of these constituents of oxalic acid, it is necessary to divide the weight of each of them by its chemical equivalent:—

$$\frac{0.476}{1} = 0.4760. \qquad \frac{1.905}{6} = 0.3175.$$

$$\frac{7.619}{8} = 0.9524.$$

These fractions are in the proportion of 2, 3, and 6; from which it follows, that the formula of the crystallized oxalic acid is $C_2\,H_3\,O_6$ or a multiple of it. Allowing the 3H to be in combination with 3O, as water, we finally obtain the formula $C_2\,O_3 + 3HO$, for the crystallized acid. [*See Supplement*, p. 772.]

CARBON AND HYDROGEN — HYDRIDES OF CARBON.

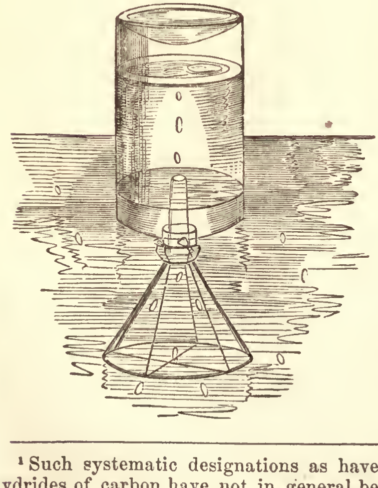
A large number of compounds of carbon and hydrogen are known; many of them found in the organic kingdom, and others derived from the decomposition of organic compounds. Some of these are liquid bodies, some solid, and others gaseous. At present we shall confine ourselves to the three gaseous compounds which in simplicity of composition resemble inorganic compounds.

PROTOCARBURETTED HYDROGEN.

Syn.[1] *Light carburetted hydrogen, Gas of the Acetates, Marsh-gas, Fire-damp.*

Eq. 16, or 200; $C_2\,H_4$; *density* 559.6; *combining measure* ⊞.

FIG. 126.



This gas is a constant product of the putrefactive decomposition of wood and other compounds of carbon, under water, and is most readily obtained by stirring the mud at the bottom of stagnant pools, and collecting the gas as it rises in an inverted bottle and funnel (fig. 126). It always contains 10 or 20 per cent. of carbonic acid, which may be separated from it by lime-water, and a small proportion of nitrogen. This gas also issues, in some places, in considerable quantities from fissures in the earth, coming often from subterraneous deposits of coal; and in the working of coal-mines it is found pent up in cavities, and would appear sometimes to be discharged from the fresh surface of the coal in sensible quantity. Hence, this gas is sometimes described as the inflammable

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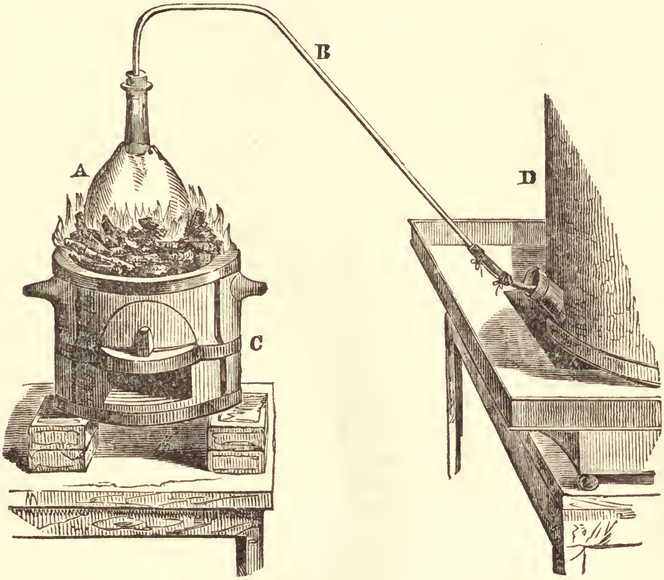
[1] Such systematic designations as have hitherto been applied to this and a few other hydrides of carbon have not in general been clear, and involve the serious error of representing the carbon as the negative element.

air of marshes, and the fire-damp of mines. It is also the most considerable constituent of coal gas, and of the gaseous mixture obtained on passing the vapour of alcohol through an ignited porcelain tube.

Preparation. — This gas is obtained by distilling a mixture of dried acetate of soda, hydrate of potassa and quicklime, in a coated glass retort. Four ounces of cr. acetate of soda may be dried on a sand-bath till anhydrous; the salt is then reduced to powder, and intimately mixed with four ounces of sticks of caustic potassa and six ounces of quicklime, both well pounded. A Florence oil flask, or other flask of hard glass, is coated with a mortar composed of a mixture of Paris-plaster, and half its weight of sand and coal-ashes, A (fig. 127); and provided with a perforated cork and bent tube B, one extremity of which should descend three or four inches in the neck of the flask. The materials above being introduced into the flask, the latter is placed in an open charcoal furnace C, and strongly heated. The gas comes off, and may be collected in jars over the pneumatic trough, or received in a gas-holder D filled with water.

Fig. 127.



Properties. — The observed density of protocarburetted hydrogen is 559.6; it is composed of 4 volumes carbon vapour, and 8 volumes hydrogen, condensed into 4 volumes, which are the combining measure of this gas. Hence its specific gravity is by calculation —

$$\frac{416 \times 4 + 69.26 \times 8}{4} = 554.5.$$

It is inodorous, neutral, respirable when mixed with air, not more soluble in water than pure hydrogen, and has never been liquefied. This carburetted hydrogen requires twice its bulk of oxygen to burn it completely, and affords water and an equal bulk of carbonic acid. The oxidation of this gas mixed with oxygen is not determined, at the temperature of the air, by spongy platinum or platinum black. In air it burns, when lighted, with a strong yellow flame. It is a compound of considerable stability, but is decomposed in part when sent through a tube heated to whiteness, and resolved into carbon and hydrogen. This gas is not affected in the dark by chlorine, but when the mixture of these gases, in a moist state, is exposed to light, carbonic and hydrochloric acid gases are produced.

Although instantly kindled by flame, protocarburetted hydrogen requires a high temperature to ignite it. Hydrogen, hydrosulphuric acid gas, and olefiant gas, and carbonic oxide, are all ignited by a glass rod heated to low redness, but glass must be heated to bright redness or to whiteness, to inflame this gas. Sir H. Davy discovered that flame could not be communicated to an explosive mixture of the gas of mines and air, through a narrow tube, because the cooling influence of the sides of the tube prevented the gaseous mixture contained in it from ever rising to the high temperature of ignition. A metallic tube had a greater cooling property, from its high conducting power, and consequently obstructed to a greater degree the passage of flame, than a similar tube of glass; and even the meshes of metallic wire-gauze, when they did not exceed a certain magnitude, were found to be impermeable by flame. Experiments of this kind may be made upon coal-gas, the flame of which will be found incapable of passing through a sheet of iron-wire trellis, containing not less than 400 holes in the square inch. If the gas be allowed to pass through the trellis, and kindled above it, the flame, it will be found, does not return through the apertures to the jet whence the gas issues. Upon these observations, Sir H. Davy founded his invaluable invention of the Safety-lamp, — an instrument now indispensable to the safe working of the most extensive and valuable of our coal-fields.

Safety-lamp. — As left by Davy, this is simply an oil lamp, enclosed in a cage of wire-gauze, the upper part of which is double (fig. 128). Mr. Buddle used iron-wire gauze for the lamp, containing from 784 to 800 holes in the square inch. A crooked wire, which works tightly in a narrow tube passing upwards through the body of the lamp, affords the means of trimming the wick, without undoing the wire-gauze cover of the lamp. When the lamp is carried into an atmosphere charged with fire-damp, a blue flame is observed within the gauze cylinder, from the combustion of the gas, and the flame in the centre of the lamp may be extinguished. The miner should then withdraw, for although the gauze has often been observed to become red-hot, without inflaming the external explosive atmosphere, yet the texture of the gauze may be destroyed, if retained long at so high a temperature. It has always been known, since this lamp was first proposed, that when it is exposed to a strong current of the explosive mixture, the flame may pass too quickly through the apertures of the gauze to be cooled below the point of ignition, and, therefore, communicate with the external atmosphere. But this is easily prevented by protecting the lamp from the draught, and an accident from this cause is not likely to occur in a coal-mine.[1]

Fig. 128.

The carburetted hydrogen does not explode when mixed with air in a proportion much above or below the quantity necessary for its complete combustion. With 3 or 4 times its volume of air it does not explode at all, with 5½ or 6 volumes of air it detonates feebly, and with 7 to 8 most powerfully. With 14 volumes of air, the mixture is still explosive, but with larger proportions of air, the gas only burns about the flame of the taper. The large quantity of air which is then mixed with the gas absorbs so much heat as to prevent the temperature of the gaseous atmosphere from rising to the point of ignition.

Coal-gas. — The products of the distillation of coal in an iron retort are of three kinds: a black oily liquid, of a heterogeneous nature, known as coal-tar; a watery

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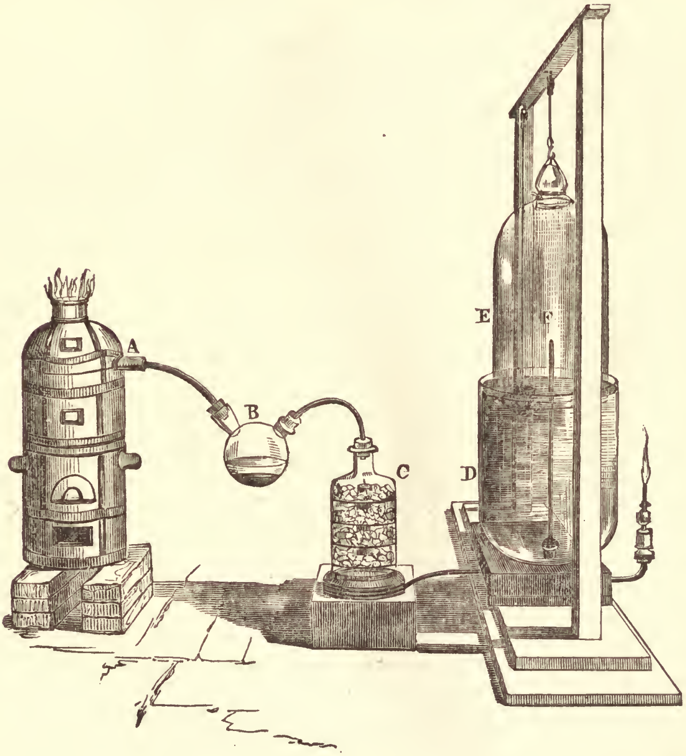
[1] For additional information respecting the safety-lamp, the reader is referred to Davy's Essay on Flame, to Dr. Paris's Life, and Dr. J. Davy's Life of Sir H. Davy, and to the Report of the Parliamentary Committee on Accidents in Mines, 1835.

fluid, known as the ammoniacal liquor, and the elastic fluids which form coal-gas. To purify the gas, it is cooled by transmitting it through iron tubes or shallow boxes, in which it deposits some condensible matter; and it is afterwards exposed to milk of lime, to absorb hydrosulphuric acid gas, which it invariably contains, and frequently afterwards to dilute sulphuric acid or a solution of sulphate of iron, which arrests a little hydrosulphate of ammonia and a trace of hydrocyanic acid. The hydrate of lime is often applied in the state of a damp powder, and not diffused through water.

The process may be illustrated by the arrangement represented in fig. 129. The coal to be distilled is contained in an iron or stoneware retort A, which should not be

Fig. 129.



more than half filled if the coal is of a bituminous quality, and is heated by a small charcoal furnace. Tar and a watery fluid containing ammonia condense in B, which represents the condenser. The gas passes on to C, a glass jar, with stages of wire-gauze supporting slaked lime, and forming a lime-purifier. The gas is then conveyed by the tube F into the bell-jar E, filled with water, and inverted over another glass jar D, serving as a water-tank. The jar E, which represents the gasometer, is connected by a string passing over two pulleys above, with an iron weight which balances it. When the gasometer rises and is full, the gas may be allowed to escape by the tube F and the jet and stopcock at the side, by removing or diminishing the counterpoise to the jar E.

Dr. Henry obtained the following results from an examination of the gas from the best cannel coal, at different periods of the distillation: —

COAL GAS IN 100 VOLUMES.

	Density.	Olefiant gas.	Carburetted hydrogen.	Carbonic oxide.	Hydrogen	Nitrogen
At beginning of process...	650	13	82.5	3.2	0	1.3
After five hours............	500	7	56	11	21.3	4.7
After ten hours..............	345	0	20	10	60	10

Besides the constituents mentioned, coal-gas, when first made, contains small quantities of

Ammonia	Hydrocyanic acid
Hydrosulphuric acid	Bisulphide of carbon
Carbonic acid	Naphtha vapour.[1]

All of these bodies are separated from it in the process of purification, except the two last, namely, naphtha vapour, which is the chief cause of the odour of coal-gas, and bisulphide of carbon, which affords a little sulphurous acid when the gas is burned. The heterogeneous nature of the gaseous mixture is well shown upon introducing a quantity of dry iodine into a bottle of coal-gas, when several liquid and solid compounds of iodine are formed with the different carbohydrogens present. Iodine, on the other hand, is not affected in the slightest degree by fire-damp, but remains with its metallic lustre unchanged in that gas. Indeed, in the ordinary fire-damp no other combustible gas whatever can be found, besides protocarburetted hydrogen (Mem. of Chem. Soc. iii. 7).

The superiority of coal-gas, in illuminating power, depends principally upon the high proportion of olefiant gas and the denser carbohydrogens which it contains. The free hydrogen and carbonic oxide present give no light, and are positively injurious. As the highly illuminating constituents are dense, and contain much carbon, the value of coal-gas is to a certain extent proportional to its density, and to the quantity of oxygen which it requires for complete combustion. In the analysis of coal-gas, the different gases may thus be separated: 1st. Olefiant gas, naphtha vapour, and similar carbohydrogens, by mixing the gas over water, in a dark place, with half its bulk of chlorine, and afterwards washing with caustic potassa; or, by introducing a small pellet of coke charged with fuming sulphuric acid and attached to a platinum wire, into the gaseous mixture, over mercury, and afterwards absorbing the acid vapour by a fragment of hydrate of potassa: 2dly, carbonic oxide, by potassium gently heated in the gas; 3dly, the proportion of protocarburetted hydrogen gas may be determined by detonating the mixture over mercury, in an eudiometer (fig. 113, page 249), with a measured quantity of oxygen, and ascertaining the quantity of carbonic acid formed, which retains the volume of this carburetted hydrogen; 4thly, the free hydrogen, by observing the quantity of oxygen remaining, by means of a stick of phosphorus introduced into the gas, and thereby ascertaining the quantity of oxygen consumed in the last combustion; from this quantity deduct twice the measure of the carburetted hydrogen found, and half the remaining measure of consumed oxygen represents the hydrogen; 5th, the residuary gas after these processes is the nitrogen of the coal-gas.[2]

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[1] Dr. Henry's Papers on Coal-Gas are contained in the Philosophical Transactions for 1808, 1820, and 1824.

[2] The tubes and eudiometers for measuring gases require to be very minutely graduated: this is attained with peculiar accuracy and facility by the method recommended by Professor Bunsen. His instrument for graduating glass tubes (fig. 130) consists of a mahogany board A, 5½ feet long, 7 inches wide, and ¾ of an inch thick. In the middle of this board is a groove extending its whole length, 1 inch wide, ½ inch deep, and rounded at bottom as a bed for the reception of the tube. At one part, 5 inches from the end, is placed a brass plate B, 1½ foot long and 2 inches wide, in such a position that when screwed down its edge comes one-half over the groove. It is furnished with four screw-nuts, passing through slits

Structure of flame.—The quantity of light obtained from the combustion of coal-gas depends entirely upon the manner in which it is burned, which will appear

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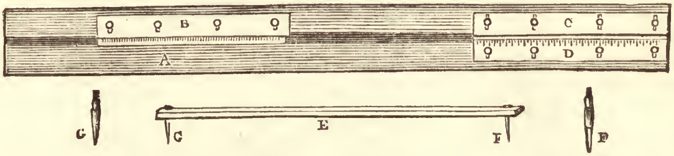
in the plate, a quarter of an inch long, so as to allow a certain advancement or withdrawal of the plate at pleasure.

Fig. 130.



C and D are two similar plates, placed at the other end of the wooden board, C having the same amount of motion as B, and being precisely similar in every respect. D is a brass plate of the same dimensions as B and C, which is cut, at intervals of five millimeters, into notches, every alternate one being one-twentieth and one-tenth of an inch deep. There is also a wooden rod E, 3 feet long, 1 inch broad, and half an inch thick. This is provided with two steel points, placed by screws at half an inch from either end. One of these, F, is in the form of a knife, the other, G, of a bradawl; a screw-driver is also provided, that these points may be attached or removed at pleasure.

Fig. 131.

When a tube is to be graduated, it is covered with a thin layer of melted wax and turpentine, by means of a camel's hair pencil, and is laid in the groove between C and D, which are then screwed down in their places, so as to retain the tube firmly in its position. A standard tube, previously mathematically divided into millimeters, (the most convenient division,) is now placed in the groove under B, (fig. 131) which is then screwed upon it. The rod, E, is now used, the pointed steel, G, being put into one of the millimeter marks on the standard tube; the knife point, F, falls upon the waxed tube, and is made to produce a line upon it, the length of which is regulated by the distance between the edges of the brass plates C and D. The pointed steel is now removed back one millimeter on the standard tube, and the corresponding mark made on the waxed one; and thus we proceed until the whole of the waxed tube is divided into millimeters. The object of the notches is, that a longer mark may be made at every five millimeters, and a still longer one at every ten, in order to aid the eye in reading. The waxed tube is now removed to a leaden trough containing pounded fluor spar and sulphuric acid, slightly heated, which etches it more successfully than a solution of hydrofluoric acid. Previously, however, to being etched, it is desirable to figure the number of millimeters at the space of every ten; and this is conveniently done by the steel pointer G, after being removed from the rod E. The tube is rubbed with vermilion powder when in use, to make the graduation more legible.

We have thus an accurate measure of length etched upon the tube, which should be one of pretty uniform calibre. The next point is to determine the true value of each of the divisional marks: this is done by calibrating it throughout all its length by small portions of mercury,—say equal in bulk to five grains of water. By this means the relative value of each mark is determined, and the proportion which it bears to any given standard. The only possible error is in the assumption that the tube is of even calibre within the space occupied by one measure of mercury; but the quantity of this added is so small, that any such error becomes quite inappreciable. The convenience of this graduator is so great, that a long tube may be beautifully divided in the course of an hour. The standard tube should be made of glass, but the original divisions from which this standard is taken may be those of wood or any other material.

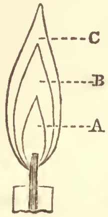
The tubes recommended by Bunsen are 18 or 19 inches in length, about 0.6 inch in internal, and 0.8 inch in external diameter. One of these is converted into a eudiometer, in which the gases are exploded, by inserting near the closed end, by fusion, two platinum wires of the thickness of horse-hair, for the purpose of passing the electric spark. During the explosion the open end of the tube is pressed firmly upon a smooth pad of caoutchouc, placed under the mercury at the bottom of the pneumatic trough. The graduation of these tubes being linear, enables the observer to read off the difference in height between the mercury in the tube and trough, and to make the necessary correction on the volume measured; all exact experiments on gaseous volumes must be made over mercury. This department of chemical analysis has been brought to a high degree of accuracy and perfection by Professor Bunsen. (See Reports of the British Association, 1845, page 148; and Liebig and Poggendorff's Handwörterbuch der Chemie, ii. 1053.)

from the consideration of the structure of luminous flames. The flame of a spirit-lamp, candle, or gas-jet, is hollow, as may be observed by depressing a sheet of wire-trellis upon it, which gives a section of the flame; the seat of the combustion being the margin of the flame, where alone the combustible vapour is in contact with the air. Of volatile carbonaceous combustibles, the flame consists of three parts, which are represented in section (fig. 132):—

A, cone of vapourized combustible.
B, sphere of partial combustion.
C, sphere of complete combustion.

In B, where the supply of air is insufficient for complete combustion, it is the hydrogen principally which burns, the carbon being liberated in solid particles, which are heated white-hot from the combustion of that gas. The sphere B, indeed, is the luminous portion of the flame, for the light depends entirely upon the deposition of carbon arising from the consecutive combustion of the two elements of the vapour. Gaseous bodies, however strongly heated, emit no light, or at most not more than a sensible glow, and luminous flame has justly been described by Davy as always containing *solid matter heated to whiteness.* The same sphere of the flame, possessing an excess of combustible matter at a high temperature, takes oxygen from metallic oxides, such as arsenious acid, placed in it, and developes their metals. It is, therefore, often referred to as the deoxidizing or reducing flame. In the external hollow cone, C, the deposited carbon meets with oxygen, and is entirely consumed. The hottest point in the whole flame is within this sphere, near the summit of B. This part of the flame, possessing an excess of oxygen at a high temperature, is the proper place for kindling a combustible, and is called the oxidizing flame: its properties are the opposite of those of B.

Fig. 132.



When coal-gas is mingled with an equal bulk of air before being burned, it is found to lose half its illuminating power. It may be conveniently mixed with a quantity of air sufficient for its complete combustion, by placing over an argand burner, a brass chimney of 5 inches in height provided with a cap of wire-gauze; when kindled above the wire-gauze, the gas burns with a blue flame, not more luminous than that of sulphur. The flame is so feebly luminous because no deposition of carbon occurs in it. The quantity of heat is the same, whether the gas is burned so as to produce much or little light; and where the gas is burned for heat, this mode of combustion has the advantage of giving a flame without smoke. The heat derived from coal-gas burned in this manner is not, however, so intense as that of an argand spirit-lamp.

A result of the circumstances which determine the quantity of light from different flames is, that the larger the flame till it begins to be smoky, the greater the proportion of light obtained from the consumption of the same quantity of gas. It was observed that an argand burner, supplied with 1½ cubic feet of gas per hour, gave as much light as a single candle; with 2 cubic feet per hour the light was equal to 4 candles, and with 3 cubic feet to 10 candles. Hence argands, bat-wings, and other burners, in which a considerable quantity of gas is burned together, are more economical than plain jets. The brightness of ordinary flame, which depends essentially upon the consecutive combustion of hydrogen and carbon, is increased by everything which promotes the rapidity and intensity of the combustion, without deranging the order of oxidation, such as a rapid supply of air, and the substitution of pure oxygen for air, as in Gurney's Bude Light. Not only is there then more light, because there is more combustion in the same time, but the temperature of the flame being greater, the luminous carbon is also heated to a higher degree of whiteness.

[*See Supplement,* p. 772.]

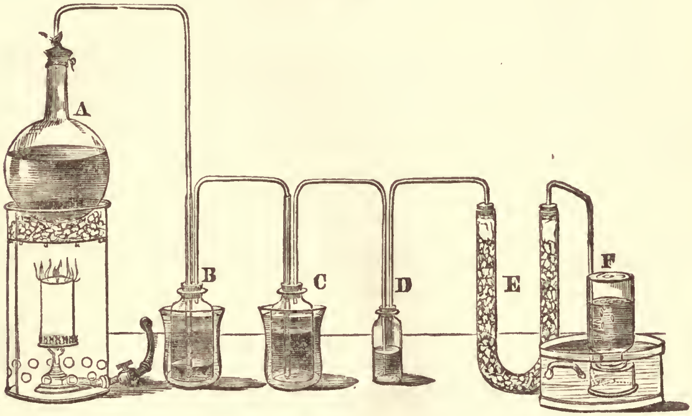
BICARBURETTED HYDROGEN.

Syn. Olefiant gas, Elayle; Eq. 28 *or* 350; C_4H_4; *density* 985.2; ☐☐

This gas was discovered in 1796, by certain associated Dutch chemists, who gave it the name of olefiant gas, because it forms with chlorine a compound having the appearance of oil. It is usually prepared by heating together 1 measure of spirits of wine with 3 measures of oil of vitriol, in a capacious retort, till the liquid becomes black and effervescence begins, and maintaining it at that particular temperature. It is collected over water, which deprives it of a portion of ether vapour and sulphurous acid, with which it is accompanied. [*See Supplement,* p. 771.]

A process which yields a purer gas, and in larger volume, is the following. Twenty-eight ounces of water are added to twice their volume of oil of vitriol, in a large globular flask A (fig. 131), which gives an acid of about 1.6 density when cool. Without waiting to cool, however, 24 ounce measures of spirits of wine are added, and the whole allowed to stand for a night. The flask is supported on a bed of pumice over the gas-flame as already described (page 264), and the latter regulated so as to keep the liquid in a state of moderate ebullition. The gas evolved is passed through two two-pound bottles, B and C, the first of which, B, is empty, or contains only a little water at the beginning, and is intended for the condensation of a considerable portion of alcohol and ether which distil over, while C is half filled with a strong solution of caustic potassa, to absorb the sulphurous and carbonic acids produced. These two wash-bottles are immersed in jars containing cold water. The third wash-bottle, D, contains oil of vitriol, and the U-tube E, pumice soaked in the same fluid to absorb ether-vapour; while the gas is collected at last in bottles, F, over water made sensibly alkaline by caustic potassa.

Fig. 133.



This gas is formed by a peculiar decomposition of alcohol, in contact with sulphuric acid boiling at 325°, or a little higher, in which the alcohol is resolved into olefiant gas and water, $C_4H_5O_2 = C_4H_4$ and 2HO. This decomposition will be referred to again more particularly under the head of alcohol.

Bicarburetted hydrogen gas contains 2 volumes of carbon vapour and 2 volumes of hydrogen condensed into 1 volume, and is theoretically of the same density as nitrogen and carbonic oxide, or fourteen times heavier than hydrogen. It was condensed by cold and pressure into a transparent liquid, which is not solidifiable (page 79). This gas, when carefully deprived of ether, has a sweet odour, which is peculiar but not strong. Water absorbs about one-eighth of its volume of this gas;

alcohol takes up 2 volumes, oil of turpentine 2.5, and olive oil 1 volume. It is absorbed by fuming sulphuric acid, and by the perchloride of antimony, forming peculiar compounds. The substances named leave certain gaseous impurities uncondensed, which often amount to 15 or 20 per cent., and appear to be principally protocarburetted hydrogen. The gas of the process described above is entirely absorbed by the perchloride of antimony, except about 4 per cent.; but it appears to contain the vapour of some denser carbohydrogen, not absorbed by oil of vitriol, as the specific gravity of the gas so prepared is often as high as that of air, or 1000, instead of 985.2 as observed by Saussure.

This gas burns with a white flame, which is much more brilliant than that of protocarburetted hydrogen. It requires three times its volume of oxygen to burn it completely, and yields twice its volume of carbonic acid gas and twice its volume of aqueous vapour; for one volume of bicarburetted hydrogen contains 2 volumes of carbon vapour, each of which requires 1 volume oxygen and becomes 1 volume carbonic acid, and 2 volumes hydrogen, each of which requires ½ volume oxygen and forms 1 volume steam. This gas is entirely decomposed, when passed through a porcelain tube at a white heat, into carbon, which is deposited, and twice its volume of hydrogen gas.

Bicarburetted hydrogen mixed with twice its volume of chlorine gas is condensed, and forms a liquid compound of an oily consistence, $C_4H_4Cl_2$, from which it was named olefiant gas, or the oil-making gas, and Elayle (from ἐλαιον and ὑλη, the source of an oil), by Berzelius. This substance, which is also known as Dutch liquid, will be described under the derivatives of alcohol. [*See Supplement*, p. 772.]

GAS OF OIL.

Bicarburetted hydrogen of Faraday; Eq. 56 *or* 700; C_8H_8; *density* 1926.4; 

This gas, which is twice as condensed as olefiant gas, is one of the products of the decomposition of the fixed oils by heat, and exists, therefore, in the gas prepared from oil. It is liquefied when oil gas is greatly compressed, and also by a cold of 0° F. The flame of this gas is very brilliant; it is only sparingly soluble in water, but pretty soluble in alcohol and the fat oils; sulphuric acid dissolves a hundred times its volume. It combines with an equal volume of chlorine, and forms a liquid compound having some analogy to Dutch liquid.

This gas requires 6 volumes of oxygen to burn it, and gives rise to water and 4 volumes of carbonic acid.

CARBON AND NITROGEN—CYANOGEN.

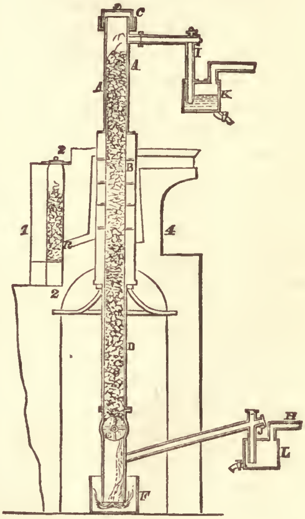
Eq. 26 *or* 325; NC_2; *density* 1819; 

This compound is a gas, which was first obtained by Gay-Lussac in 1815. It is prepared by heating the cyanide of mercury in a small glass retort, and is collected at the mercurial trough. The cyanide is resolved into running mercury and cyanogen gas, and frequently leaves a black coaly mass in the retort, which Professor Johnston has shown to consist of carbon and nitrogen, in the same proportions as the gas itself.

Cyanogen gas contains 4 volumes of carbon vapour and 2 volumes of nitrogen, condensed into 2 volumes; its density is 1819. When this gas is exploded with twice its volume of oxygen, it affords 2 volumes of carbonic acid gas, and 1 volume of nitrogen; an experiment from which its composition may be deduced. Water at 60° absorbs 4.5 times its volume of this gas, and alcohol 23 volumes. By a pressure of 3.6 atmospheres at 45°, cyanogen is condensed into a limpid liquid, which evaporates again on removal of the pressure. Cyanogen burns with a beautiful purple flame in air or oxygen. The solution of cyanogen in water undergoes spontaneous decomposition. By alkalies the gas is absorbed, and a cyanide and cyanate formed.

Carbon does not burn when heated in nitrogen gas, and appears to be incapable of uniting with that element when alone, or unless when assisted by the presence of a third body, such as potassium, which unites with and gives stability to the compound. Cyanogen is thus produced when nitrogen is sent over fragments of charcoal saturated with potassa, heated white-hot in a porcelain tube placed across a furnace, and obtained as cyanide of potassium. A peculiar form of furnace, in which this remarkable process is conducted on a large scale at Newcastle, with considerable success, is described by Mr. Bramwell (Repertory of Inventions, 3 ser. ix. 280). It consists essentially of a vertical flue in brickwork A B D, (fig. 134), containing charcoal charged with a solution of carbonate of potassa, the middle portion of which, B, is placed within the flue of the adjoining furnace 2 2, by which it is heated intensely, and also obtains a supply of nitrogen, which enters A B D by a number of small openings into the external flue. The passage of gases upwards through the potassa-charcoal is further promoted by the action of air-pumps connected with the tubes G and H. The materials are introduced at the top on removing a lid C, and after descending through the tube are allowed to fall into a cistern of water F, in which the cyanide of potassium is found dissolved. The pipes I and J dip into water, to intercept ammonia or any other volatile product.

Fig. 134.



Cyanogen is a salt-radical, and unites with all the metals, as chlorine and iodine do, forming a class of cyanides. It also combines with hydrogen and forms a hydrogen-acid, namely, hydrocyanic or prussic acid. Cyanogen properly belongs to organic chemistry, in which department its numerous combinations will be considered.

Mellon, N_4C_6.—This is another salt-radical, and was formed by Liebig by heating the bisulphide of cyanogen in a glass flask to redness, when it is resolved into sulphur, bisulphide of carbon, and mellon. It is a lemon yellow powder, insoluble in water and alcohol; it unites directly with hydrogen and with potassium, forming hydro-mellonic acid, a hydrogen-acid, and mellonide of potassium, a saline body.

SECTION V.

BORON.

Eq. 10.9 *or* 136.2; B; *density of vapour* (*hypothetical*) 751; ☐☐ .

Boron is an element having some analogy to carbon, but sparingly diffused in nature. It is never found, except in combination with oxygen as boracic acid, of which the salt of soda has long been brought to Europe from India in a crude state, under the name of tinkal, and termed borax when purified. The impure borax or tinkal forms a saline incrustation in the beds of certain small lakes in an upper province of Thibet, which dry up during summer. But the most considerable of the present sources of boracic acid are the hot lagoons of a district in Tuscany, which are charged with the free acid, from the condensation in them of vapours of a volcanic origin. Boracic acid is likewise found in the hot springs of Lipari. It is a constituent also of several minerals, of which datolite and boracite are the most remarkable. Boron was first discovered by Sir H. Davy in 1807, by exposing boracic acid to the action of a powerful voltaic battery, and was afterwards obtained by Gay-Lussac and Thenard in greater quantity, by heating boracic acid with potassium. [*See Supplement*, p. 773.]

Preparation.—Boron is prepared with greatest advantage from a combination of fluoride of boron and fluoride of potassium, which is obtained on saturating hydrofluoric acid with boracic acid, and afterwards adding to it, drop by drop, the fluoride of potassium. This compound, which is of slight solubility, is collected on a filter, and dried at an elevated temperature, but which should not reach a red heat. Equal weights of the compound and of potassium are mixed together in a cylinder or tube of iron, closed at one end, which is gently heated, and the mixture stirred with an iron rod, till the potassium is melted. Heated afterwards more strongly by a spirit-lamp, the mass evolves heat, and becomes red-hot; the potassium combines with the fluorine, and a mixture is obtained of boron and the fluoride of potassium. On treating this with water, the fluoride of potassium dissolves, and the boron remains alone. In washing it farther, instead of pure water, which causes the oxidation of boron, a solution of sal ammoniac should be employed, which does not act upon that body, and the sal ammoniac remaining in the boron may be taken up by alcohol.

Properties.—Thus prepared, boron is obtained in the form of a greenish-brown powder, without the metallic lustre, which becomes hard and assumes a deeper colour, when ignited in vacuo, or in gases which do not combine with it, but undergoes no farther change. Heated in atmospheric air or oxygen it burns with a vivid light, scintillating powerfully, and forms boracic acid. Nitric acid and many other substances also oxidate it easily, and always produce that compound. Fused with carbonate of potassa, it decomposes the carbonic acid, and gives borate of potassa, carbon being liberated. Boron is not known to possess any other degree of oxidation. Boron combines with sulphur, with the disengagement of light, when heated in the vapour of that substance; and it takes fire spontaneously in chlorine, and forms a gaseous chloride of boron, of which the formula is BCl_3, and the density 3942 by observation and 4035 by calculation. This gas is composed of 2 vols. of boron vapour and 6 of chlorine, condensed into 4 vols., which are its combining measure. It may likewise be formed by transmitting chlorine gas over a mixture of boracic acid and charcoal, ignited in a porcelain tube. A corresponding fluoride of boron is evolved from boracic acid, ignited with the fluoride of calcium or fluor-spar, with the formation of borate of lime. The density of this fluoride is 2312.4. Both of these gases are decomposed by water, boracic acid being formed with hydrochloric or hydrofluoric acid.

Boracic or Boric acid.—This acid is prepared by dissolving the salt borax at 212° in two and a half times its weight of water, and adding enough of hydrochloric acid to make the liquid strongly acid to test paper. Chloride of sodium is formed, which continues in solution, while the boracic acid separates in thin shining crystalline plates, on cooling. These plates are drained, and being sparingly soluble, may be washed with a little cold water, and afterwards redissolved in boiling water, and made to crystallize anew. Fused at a red heat in a platinum crucible, these plates give the vitrified acid, of which the density is 1·83. Boracic acid has a weak taste, which is scarcely acid, and it affects blue litmus like carbonic acid, imparting to it a wine-red tint, and not that clear red, free from purple, which the stronger acids produce. It renders yellow turmeric paper brown, like the alkalies. The acid of the carbonates, however, is displaced by boracic acid in the cold, and at a red heat this acid decomposes even the sulphates, from its comparative fixity. The crystals of boracic acid are a hydrate, and contain 3 equivalents of water, of which the formula is $HO.BO_3+2HO$. At 60° it requires 25.66 times its weight of water to dissolve it, but only 2.97 times at 212°. With the assistance of the vapour of water, it is slightly volatile, but alone it is more fixed, and fuses, under a red heat, into a transparent glass. At the white heat of our furnaces boracic acid does not boil; but the tension of its vapour is so considerable at that temperature that it evaporates entirely away in the end. The hydrated acid dissolves in alcohol, and the solution burns with a fine green flame. It communicates fusibility to many substances in uniting with them, and generally forms a glass. On this account borax is much used as a flux.

Borates. — Boracic acid is remarkable for the variety of proportions in which it unites with alkalies; all these borates have an alkaline reaction like the carbonates. The relative proportions of oxygen and boron in boracic acid are known, but the number of equivalents of these elements in this acid is not so certain. Dumas inferred from the density of the chloride that it is a terchloride, and boracic acid, which corresponds, will therefore consist of 3 eq. of oxygen to 1 eq. of boron, and its formula be BO_3. This makes borax the biborate of soda. [*See Supplement*, p. 774.]

SECTION VI.

SILICON OR SILICIUM.

Eq. 21.35 *or* 266.82; Si; *density of vapour (hypothetical)* 1475; ◫

Silica or siliceous earth, the oxide of the present element, is the most abundant of all the matters which compose the crust of the globe. It constitutes sand, the varieties of sand-stone and quartz rock, and enters into felspar, mica, and a great variety of minerals, which form the basis of other rocks. [*See Supplement*, p. 776.]

Preparation. — Silica may be decomposed by heating it with potassium, which deprives it of oxygen; but a better process for obtaining silicon is to heat the double fluoride of silicon and potassium, with 8 or 9-10ths of its weight of potassium, with the same precautions as in the preparation of boron. The materials, however, in this case may be heated in a glass tube, as well as in an iron cylinder. The double fluoride employed is prepared by neutralizing fluosilicic acid with potassa. A different process is suggested by Berzelius, which consists in heating potassium in a tube of hard glass with a small bulb blown upon it, which is filled with the vapour of the fluoride of silicon, supplied from the ebullition of that liquid contained in a small retort connected with the glass tube. The potassium burns in this vapour, and at the end, silicon is found, with fluoride of potassium, in the place of the metal (Traité, t. 1, p. 307). But the silicon from all these processes is always in combination with a little potassium, and mixed with a little fluoride of silicon and potassium unreduced. Hence, on applying cold water to the mass, hydrogen gas is disengaged, and potassa formed, and the silicon separates. The potassa thus produced can, with the aid of hot water, dissolve the silicon, which then oxidates and becomes silica, so that cold water only must be employed to wash the silicon, which may be thrown upon a filter. After a time, the liquid which passes has an acid reaction, which arises from its dissolving an acid double fluoride of silicon and potassium, of sparing solubility, which has escaped decomposition, and is mixed with the silicon. The washing is continued so long as the water dissolves anything.

Properties. — The silicon which is thus obtained is, in its pure state, a dull brown powder, which soils the fingers, and when heated in air or oxygen, inflames and burns, but is never more than partially converted into silica. It may be ignited strongly in a covered crucible without loss, and then shrinks in dimensions, acquires a deep chocolate colour, and becomes so dense as to sink in oil of vitriol. By this ignition the properties of silicon are altered to a degree which is very remarkable in a simple substance. It was previously readily soluble in hydrofluoric acid, with evolution of hydrogen, and in caustic potassa, but it is now no longer acted upon by that or any other acid, nor by alkalies. The ignited silicon also refuses to burn in air or oxygen, even when intensely heated by the blowpipe flame. Charcoal, it will be remembered, is more dense and less combustible after being strongly heated; but that substance is not altered by heat to the same extent as silicon. Mixed and heated with dry carbonate of potassa, silicon in any condition is oxidated completely, its action upon the carbonic acid of the salt being attended with ignition, and carbon liberated. Silicon burns when heated in sulphur vapour, and forms a sulphide, which water dissolves, but decomposes at the same time, hydrosulphuric acid and silica being produced, and the last, notwithstanding its usual insolubility, retained in solution. Silicon likewise burns in chlorine; and the chloride of silicon may be otherwise formed by transmitting chlorine over a mixture of charcoal and silica ignited in a porcelain tube. The silica is decomposed by neither charcoal nor chlorine singly, but acting together upon the silica, these bodies produce carbonic oxide and chloride of silicon. This compound is a volatile liquid, of which the formula is $Si\ Cl_3$; that of the sulphide of silicon $Si\ S_3$.

Silica or Silicic Acid, $Si\ O_3$. — This earth, which is the only oxide of silicon, constitutes a number of minerals, nearly in a state of purity, such as rock-crystal, quartz, flint, sandstone, the amethyst, calcedony, cornelian, agate, opal, &c. The first chemical examination of its properties and compounds is due to Bergman.

Preparation. — Silica may be had very nearly, if not absolutely pure, by heating a colourless specimen of rock-crystal to redness and throwing it into water, after which treatment the mineral may be easily pulverized. It is obtained in a state of more minute division, by transmitting the gaseous fluoride of silicon (fluosilicic acid) into water; or by the action of acids upon some of the alkaline compounds of silica. Equal parts of carbonate of potassa and carbonate of soda may be fused in a platinum crucible, at a temperature which is not high; and pounded flint or any other siliceous mineral, thrown by little and little into the fused mass, dissolves in it with an effervescence due to the escape of carbonic acid gas. The addition of the mineral is continued so long as it determines this effervescence. The mass being allowed to cool, is afterwards dissolved in water acidulated with hydrochloric acid, which takes up the silica as well as the alkalies; the liquor is filtered and then evaporated to dryness. The silica may contain a little peroxide of iron or alumina, to dissolve which the saline mass, when perfectly dry, is moistened with concentrated hydrochloric acid, and after two hours the acid mass is washed with hot water. The silica remains undissolved; it may be dried well and ignited.

Properties. — Silica so prepared is a white, tasteless powder, which is rough to the touch, and feels gritty between the teeth. It is extremely mobile when heated, and is thrown out of a crucible, at a high temperature, by the slightest breath of wind. It is absolutely insoluble in water, acids, and most liquids. Finely divided silica, however, decomposes an alkaline carbonate at the boiling point, and is dissolved. Its density is 2.66. The heat of the strongest wind-furnace is not sufficient to fuse silica, but it melts into a limpid colourless glass in the flame of the oxihydrogen blowpipe, and may be drawn out into threads (Girardin). Silica is found frequently crystallized, its ordinary form being a six-sided prism terminated by a six-sided pyramid, as in rock-crystal. Sometimes the prism is very short or disappears entirely, and the pyramid only is seen, as in ordinary quartz.

Silicic acid dissolved by acids. — The conditions of the solubility of silicic acid in other acids are peculiar. Once precipitated, whether gelatinous, like boiled starch, or pulverulent, it is no longer in the least degree soluble either in water or acids. If to a dilute solution of an alkaline silicate, hydrochloric acid be added slowly and drop by drop, the silicic acid is precipitated in proportion as the alkali is neutralized. But, on the contrary, no silicic acid is precipitated, if strong hydrochloric acid in considerable excess be added all at once to the solution of alkaline silicate, or if the latter be poured in a gradual manner into hydrochloric acid whether strong or greatly diluted with water. It thus appears that silicic acid only dissolves in the stronger acids, when presented to them in the *nascent state,* or at the moment of leaving another combination. It appears to enter into combination with the acid which dissolves it; for if the latter is exactly neutralized by adding a strong solution of potassa, drop by drop, the whole of the silica is precipitated.

A pure solution of silicic acid in hydrochloric acid, free from saline matter, is best obtained from the silicate of copper. The latter is prepared by precipitating chloride of copper by the solution of an alkaline silicate; washing the insoluble silicate of copper which falls, by several times mixing it with water and allowing it to subside, so as to get rid of the chloride of potassium present. The silicate of copper is then dissolved in hydrochloric acid, filtered, and hydrosulphuric acid gas made to stream through the liquid, to precipitate the copper. The black insoluble sulphide of copper is removed by filtration, and a perfectly colourless solution of silicic acid is obtained, which may be boiled, to expel the excess of hydrosulphuric acid, without injury. This solution is very acid, and when neutralized by ammonia or potassa it allows gelatinous silica to precipitate.

Hydrates of silicic acid. — When the last solution of silica in hydrochloric acid is evaporated in vacuo over fragments of quicklime, it deposits the protohydrate of silica, $SiO_3 + HO$, in very thin crystalline filaments, grouped in stars, which are colourless, transparent, and possessed of considerable lustre. This is also the composition of the gelatinous silica, precipitated from an alkaline silicate, when allowed to dry in air. The silica has first the appearance of a transparent jelly, which is tenacious, and cracks on drying, forming a mass like gum. When this hydrate is dried at 212°, one half of the water escapes, and another definite hydrate, $2SiO_3 + HO$, remains (Doveri). Another hydrate was obtained, by M. Ebelmen, by the spontaneous decomposition of silicic ether, of which the composition is $2SiO_3 + 3HO$. At 370° C. (698° F.), silicic acid does not retain more than a trace of water. (Doveri: Observations on the Properties of Silica, Annales de Chim. et de Phys. xxi. p. 40, 1847.)

Hydrofluoric acid has an affinity quite peculiar for silica, decomposing it, and carrying off the silicon, in the form of the volatile fluoride of silicon: —

$$3HF \text{ and } SiO_3 = SiF_3 \text{ and } 3HO.$$

The water of springs and wells always contains a little soluble silica, which can only be separated by evaporating the water to dryness. In some mineral waters the proportion of silica is very considerable, and it is often associated with an alkaline carbonate, which silica is capable of decomposing at the boiling point; as in the hot alkaline spring of Reikum in Iceland, and in the boiling jets of the Geyser, which deposit about their crater an incrustation of silica. There can be no doubt likewise that much of the crystalline quartz in nature, besides all the agates, calcedonies, and silicious petrifactions, have been formed from an aqueous solution.

Silicates. — Although silica has no acid reaction, it is certainly an acid, and is indeed capable of displacing the most powerful of the volatile acids at a high temperature. It is capable of uniting with metallic oxides, by way of fusion, in a great variety of proportions. Its compounds with excess of alkali are caustic and soluble, but those with an excess of silica are insoluble, and form the varieties of *glass*, which will be described under the silicate of soda. With alumina it forms the less fusible compounds of porcelain and stoneware, which will be noticed under that earth. A large number of mineral species also are earthy silicates. It seems probable that silicic, like phosphoric acid, forms several classes of salts, of which those containing the largest number of atoms of base are the most easily decomposed by acids. At the same time, some allatropic difference may be suspected between the silicic acid itself, as it exists in these different classes of salts, such as there is between ignited and unignited silicon. [*See Supplement*, pp. 777, 778.]

The formula for silicic acid is not very certainly established. Most chemists admit it to be SiO_3, or analogous to sulphuric acid, SO_3, and then the equivalent of silicon is 266.7. But others adopt the formula SiO_2, considering silicic acid analogous to carbonic acid, CO_2; the equivalent of silicon then becomes 177.8. The last view is most in accordance with the density of silicic ether vapour. On the other hand, the composition of two intermediate compounds between the chloride of silicon, $SiCl_3$, and the sulphide of silicon, SiS_3, namely, $SiSCl_2$ and SiS_2Cl, is most simply represented on the first view. (Is. Pierre.)

SECTION VII.

SULPHUR.

Eq. 16 *or* 200; S; *at* 600°, *density of vapour* 6634, *and combining measure* 1-3d *volume; at* 1800°, *density about one-third of above, and combining measure* 1 *volume* □.

This element is exhaled in large quantity from volcanoes, either in a pure state or in combination with hydrogen, and by condensing in fissures forms sulphur veins, from which the greater part of the sulphur of commerce is derived. (See Recherches sur les fumerolles, par MM. Melloni and Piria: Annales de Chim. et de Phys. 2de sér. lxxiv. 331.) It exists also in combination with many metals, as iron, lead, copper, zinc, &c.; and is sometimes extracted from iron pyrites or bisulphide of iron. Sulphur is classed with oxygen; and the higher sulphides resemble peroxides in losing a portion of their sulphur, as some of the latter lose a portion of their oxygen, when strongly heated. Sulphur is likewise extensively diffused, as a constituent of the sulphuric acid, in gypsum and other native sulphates. This element also enters into the organic kingdom, being invariably associated in minute quantity with albuminous or protein compounds.

*Properties.**—Sulphur is found in commerce in rolls, which are formed by pouring melted sulphur into cylindrical moulds, and also in the form of a fine crystalline powder, the flowers of sulphur, which are obtained by throwing the vapour of sulphur into a close apartment, of which the temperature is below the point of fusion of that substance, and in which the sulphur therefore condenses in the solid form and in minute crystals, just as watery vapour does in the atmosphere below 32°, in the form of snow. The purity of the flowers is more to be depended upon than that of roll-sulphur. Sulphur is insipid and generally inodorous, but acquires an odour when rubbed; it is very friable, a roll of it generally emitting a crackling sound, and sometimes breaking, when held in the warm hand. Its specific gravity is 1.98. It fuses at 234°, forming a transparent and nearly colourless liquid, which is lighter than the solid sulphur. As the temperature is elevated, the liquid becomes more yellow, and passes abruptly into a dark brown at 482°. These allatropic conditions are distinguished by Frankenheim as $S\alpha$ and $S\beta$. In the last state it is so thick and viscous as to flow with difficulty. This change in its degree of fluidity is not occasioned by an increase of density, for fluid sulphur continues to expand with the temperature. Thrown into water, while in this condition, sulphur forms a mass which remains soft and transparent for some time after it is perfectly cool, and may be drawn into threads which have considerable elasticity. From 500° to its boiling point, 788°, when it is distinguished as $S\gamma$, it becomes again more fluid, and if allowed to cool returns through the same conditions, becoming again very fluid, before freezing. Sulphur has considerable volatility, beginning to rise in vapour before it is completely fused. At its boiling point it forms a transparent vapour of an orange colour, and distils over unchanged. The density of this vapour, taken a little above its boiling point, is very considerable, being observed to lie between 6510 and 6617 by Dumas, to be 6900 by Mitscherlich. These results indicate the unusual combining measure of 1-3d of a volume for this vapour, which gives the theoretical density 6634. But sulphur-vapour has lately been shown by M. Bineau to be one of those bodies of which the density changes with the temperature (page 132), and to fall at 1000° C. under ordinary pressure to about one-third of what it is about 450° or 500° C. The anomaly of its density is thus removed, and the combining measure of sulphur-vapour made to be 1 volume, or the same as oxygen.

Sulphur and many other substances may be obtained in distinct crystals, on passing from a state of fusion, by operating in a particular manner. A considerable quantity of sulphur is fused in a stoneware crucible, and allowed to cool till it begins to solidify; the solid crust which covers its surface is then broken, and the portion

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* [*See Supplement*, p. 775.]

remaining fluid poured out. On afterwards breaking the crucible, when it has become quite cold, the sulphur is found to have a considerable cavity, which is lined with fine crystals, like a geode in quartz. Sulphur is dimorphous; the form which it assumes at a high temperature, and consequently in its passage from a state of fusion, is a secondary modification of an oblique prism with a rhomboidal base (fig. 135), belonging to the Fifth System of crystallization (page 144). Sulphur is soluble in the sulphide of carbon, the chloride of sulphur and oil of turpentine, and is deposited from solution in these menstrua at a lower temperature, and of its second form, which is an elongated octohedron with a rhomboidal base (fig. 136), belonging to the Third System. Such is likewise the form of the grains of flowers of sulphur, and of the fine transparent crystals of native sulphur; which last appear also to be formed by sublimation.

FIG. 135.

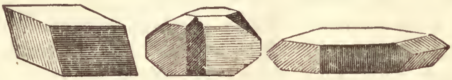
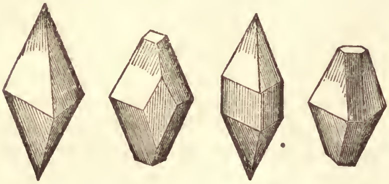


FIG. 136.



Sulphur is not soluble in water nor in alcohol. It combines readily with most metals; some of them, such as copper and silver in very thin plates, burning in its vapour, as iron does in oxygen gas. When iron and some other metals are mixed in a state of division with flowers of sulphur, and heat applied, the sulphur first melts, and after a few seconds combination ensues with turgescence of the mass, which becomes red-hot. Sulphur unites with bodies generally in the same multiple proportions as oxygen, and sometimes in additional proportions, particularly with potassium, and the metals of the alkalies and alkaline earths. When boiled with caustic potassa or lime, red solutions are formed which contain a large quantity of sulphur, a considerable proportion of which is deposited as a white hydrate of sulphur, upon the addition of an acid. With hydrogen, sulphur unites in single equivalents, and forms hydrosulphuric acid gas, which is the analogue of water in the sulphur series of compounds; and also another compound, the bisulphide of hydrogen, which is deficient in stability, like the binoxide of hydrogen, and is decomposed or preserved by similar agencies.

Sulphur is readily inflamed, taking fire below its boiling point, and burning with a pale blue flame and the formation of suffocating fumes, which are sulphurous acid gas. It exhausts the oxygen of a confined portion of air by its combustion more completely than carbonaceous combustibles, and on that account, and partly also from a negative influence which sulphurous acid has upon the combustion of other bodies, it may be employed in particular circumstances to extinguish combustion; a handful of lump sulphur being dropped into a burning chimney as the most effectual means of extinguishing it. Sulphur unites directly with oxygen only in the proportion of sulphurous acid, but several compounds of the same elements may be formed, which are all acids; namely—

1.	Sulphurous acid	$S\ O_2$
2.	Hyposulphurous acid	$S_2\ O_2$
3.	Sulphuric acid	$S\ O_3$
4.	Hyposulphuric acid	$S_2\ O_5$
5.	Monosul-hyposulphuric acid	$S_3\ O_5$
6.	Bisul-hyposulphuric acid	$S_4\ O_5$
7.	Trisul-hyposulphuric acid	$S_5\ O_5$

Uses.—From its ready inflammability sulphur has long been applied to wood matches. But its most considerable applications are in the composition of gunpowder and other deflagrating mixtures, and in the manufacture of sulphuric acid, which there will again be occasion to notice in a more particular manner.

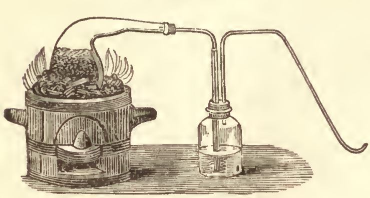
SULPHUROUS ACID.

Eq. 32 *or* 400; SO_2; *density of gas* 2247; *combining measure* ☐☐

Sulphurous acid was distinguished as a particular substance by Stahl, and first recognised as a gas by Dr. Priestley. It was subsequently analyzed with accuracy by Gay-Lussac and by Berzelius.

Preparation.—When sulphur is burned in dry air or oxygen gas, sulphurous acid is the sole product, and the gas is found to have undergone no change in volume. But sulphurous acid is more conveniently prepared in laboratories by several other processes.

Fig. 137.



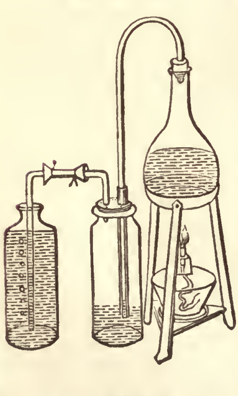
(1.) An intimate mixture of 6 parts of binoxide of manganese and 1 part of flowers of sulphur is heated in a small retort of hard glass (fig. 137;) the gas is carried through a wash-bottle to arrest a little vapour of sulphur which is carried over. Here the sulphur is burnt at the expense of a portion of the oxygen of the binoxide of manganese. Sulphurous acid, which is the product of the combustion, escapes, and protoxide of manganese remains in the retort. (Regnault).

$$S \text{ and } 2\,MnO_2 = SO_2 \text{ and } 2\,MnO.$$

(2.) By heating oil of vitriol upon mercury or copper, either of which becomes an oxide at the expense of one portion of the sulphuric acid, and thereby causes the formation of sulphurous acid. Sheet copper cut into small pieces is put into a flask to which undiluted oil of vitriol is added, and a moderate heat applied. The gas is carried through a bottle, containing a little water to condense the vapour of sulphuric acid, of which a little is carried over, and afterwards through a tube containing chloride of calcium, if it is desired to dry the gas.

(3.) Charcoal, chips of wood, straw, and such bodies, occasion a similar decomposition of sulphuric acid, when heated with it, but the gas is then mixed with a large quantity of carbonic acid. If the sulphurous acid, however, is to be used to impregnate water, or in making alkaline sulphites, the presence of that gas is immaterial. With that object, a quantity of oil of vitriol, equal in volume to 4 ounce measures of water, which for brevity may be spoken of as 4 ounce measures of oil of vitriol, is introduced into a flask with half an ounce of pounded wood-charcoal, and the two substances well mixed with agitation (fig. 138). Effervescence takes place upon applying heat to the flask, from the evolution of gas, which may be conducted in the first instance into an intermediate phial, through the cork of which a stout tube passes, open at both ends, and about 3-8ths of an inch in internal diameter. This phial contains about an ounce of water, into which the wider tube dips, and the tube from the flask descends still lower. The phial serves the purpose of a wash-bottle in condensing any sulphuric acid vapour that may be carried over by the gas, or of intercepting the liquid material in the flask, if thrown out by ebullition, and also of preventing the liquid in the second bottle from passing back, by the glass tube, into the generating flask, on the occurrence of a contraction of the air in that flask, by cooling or any other cause. When that contraction happens in this arrangement, the external air enters the intermediate phial by its open tube. The second bottle is nearly filled with water to be impregnated by the gas.

Fig. 138.



Properties.—Water at 60° is capable of dissolving nearly 50 times its volume of sulphurous acid, which makes it necessary to collect this gas for examination by displacement of air, or in jars filled with mercury in the mercurial trough. Its density is 2247, and it contains 2 volumes of oxygen with 1 volume of sulphur vapour (density 2211), condensed into 2 volumes, which form its combining measure. It may easily be obtained in the liquid state by transmitting the dry gas obtained by the first or second process through a U-shaped tube, surrounded by a freezing mixture of ice and salt, or better, of ice and chloride of calcium. It forms a colourless and very mobile liquid, of sp. gr. 1.45, which boils at 14°. The volatility of this liquid is small at considerably lower temperatures, and it is not applicable with advantage to produce intense cold by its evaporation (Kemp). Sulphurous acid crystallizes from a saturated solution in water, at a temperature of 4 or 5 degrees above 32°, in combination with 72 per cent. of water or 9 equivalents, SO_2+9HO (Pierre, Ann. de Chim. et Phys. 3 ser. 23.416).

Sulphurous acid is not decomposed by a high temperature; but several substances, such as carbon, hydrogen, and potassium, which have a strong affinity for oxygen, decompose it at a red heat. This acid blanches many vegetable and animal colours,—thus violets plunged for a short time into a solution of sulphurous acid become completely white; and the vapours of burning sulphur are therefore employed to whiten straw and to bleach silk, to which they also impart a peculiar gloss. The colours are not destroyed, and may in general be restored by the application of a stronger acid or an alkali. Dry sulphurous acid exhibits no affinity for oxygen, but in contact with a little water these gases slowly combine, and sulphuric acid is formed. From the same affinity for oxygen, sulphurous acid deprives the solution of permanganate of potassa of its red colour, and throws down iodine from iodic acid. It decomposes the solutions of those metals which have a weak affinity for oxygen, such as gold, silver, mercury (with heat), and throws down these bodies in the metallic state. Sulphurous acid is conveniently withdrawn from a gaseous mixture by means of peroxide of lead, which is converted by absorbing this gas into the white sulphate of lead. By nitric acid, sulphurous acid is immediately converted into sulphuric acid.

Sulphites.—The alkaline sulphites have a considerable resemblance to the corresponding sulphates. Their acid is precipitated by the chloride of barium, but the sulphite of baryta is dissolved by hydrochloric acid. When in solution the sulphites gradually absorb oxygen from the air, and pass into sulphates. Sulphurous acid is a weak acid, and its salts are decomposed by most other acids.

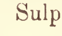
Uses.—Besides the application of which sulphurous acid is susceptible in bleaching, it is likewise employed in French hospitals, in the treatment of diseases of the skin. The gas is then applied in the form of a bath. (Dumas, Traité de Chimie appliquée aux Arts, i. 151).

This oxide of sulphur, besides acting as an acid, has been supposed to play the part of a radical, like carbonic oxide, and to pervade a class of compounds, in which hyposulphurous acid and sulphuric acid are included:—

SULPHUROUS ACID SERIES.

Sulphurous acid	SO_2
Sulphuric acid	SO_2+O
Hyposulphurous acid	SO_2+S
Chlorosulphuric acid	SO_2+Cl
Nitrosulphuric acid	SO_2+NO_2
Azotosulphuric acid	$2SO_2+NO_5$

SULPHURIC ACID.

Eq. 40 *or* 500; SO_3; *density of vapour* 2762; 

Chemists have been in possession of processes for preparing this acid since the end of the fifteenth century. It is of all reagents the one in most frequent use, being the key to the preparation of most other acids; which, in consequence of its superior affinities, it separates from their combinations; and being the acid preferred to others, from its cheapness, for various useful and important purposes in the arts.

Preparation.—Sulphuric acid was first obtained by the distillation of green vitriol or copperas, a native sulphate of iron, and this process is still followed in Bohemia, for the preparation of a highly concentrated acid, known as the Nordhausen acid, from being long produced at Nordhausen in Saxony. The sulphate of iron contains seven equivalents of water, and is first dried, by which its water is reduced considerably below a single equivalent, and then distilled in a retort of stoneware at a red heat. When the experiment is performed on a small scale, the heat of an argand spirit-lamp is sufficient; and in the place of copperas, the sulphate of iron previously peroxidized, the sulphate of bismuth, of antimony, or of mercury, may be employed. The first effect of heat upon the dried sulphate of iron is to cause an evolution of sulphurous acid gas, a portion of sulphuric acid being decomposed in converting the protoxide of iron of that salt into sesquioxide,

$$2\,(FeO.SO_3) = SO_2 \text{ and } SO_3 \text{ and } Fe_2O_3;$$

but the salt used in Bohemia, it appears, is a native sulphate, in which the greater part of the iron is already in the state of sesquioxide, so that little sulphurous acid is lost. Vapours afterwards come over, which condense into a fuming liquid, generally of a black colour, and of a density about 1.9, which is the Nordhausen acid, and contains less than one equivalent of water to two of sulphuric acid. This acid is preferred for dissolving indigo, and for some other purposes in the arts, and is the best source of anhydrous sulphuric acid.

But sulphuric acid is prepared, in vastly greater quantity, by the oxidation of sulphur. When burned in air or oxygen, sulphur does not attain a higher degree of oxidation than sulphurous acid, but an additional proportion of oxygen may be communicated to it by two methods, and sulphuric acid formed.

1. When a mixture of sulphurous acid and air, which must be previously dried, is made to pass over spongy platinum, or a ball of clean platinum wire, at a high temperature, the sulphurous acid is converted into sulphuric acid at the expense of the oxygen of the air. After a time, however, the platinum loses this property, and the process, although interesting in a scientific point of view, does not answer, on account of that change, as a manufacturing method.

2. Sulphurous acid mixed with air may be converted into sulphuric acid, by the agency of nitric oxide, which is the process generally pursued in the manufacture of this acid. The theory of this latter method, which is by no means obvious, has been illustrated by the researches of Clement-Desormes, Davy, De la Provostaye, and others. It is generally considered as depending upon the following reactions:—

1. When binoxide of nitrogen NO_2 mixes with air in excess, it is instantly converted into peroxide of nitrogen NO_4.

2. Peroxide of nitrogen is converted by contact with a small quantity of water into the nitrate of water and nitrous acid.

$$2NO_4 \text{ and } HO = HO.NO^5 \text{ and } NO_3.$$

3. Nitrous acid in contact with a large quantity of water is converted into nitrate of water and binoxide of nitrogen.

$$3NO_3 \text{ and water in excess} = HO.NO_5 + \text{Water and } 2NO_2.$$

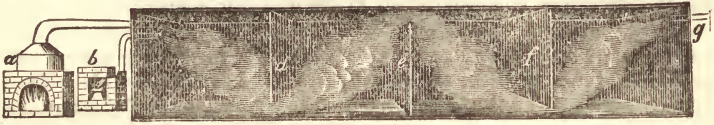
Consequently, uniting the last two operations, peroxide of nitrogen is converted by a large quantity of water into nitric acid and binoxide of nitrogen.

4. Sulphurous acid takes oxygen from hydrated nitric acid, and becomes sulphuric acid, disengaging peroxide of nitrogen.

As the peroxide of nitrogen gives nitric acid and binoxide of nitrogen (3), and the last gas is converted by air into peroxide of nitrogen (1), the production of nitric acid may be repeated without end, and more and more sulphurous acid is converted by the latter into sulphuric acid. It thus appears that with a sufficient supply of air or oxygen, a small quantity of nitric acid (or of binoxide of nitrogen) may convert a large quantity of sulphurous acid into sulphuric acid. The binoxide of nitrogen, only acting as a purveyor of oxygen, is re-obtained entire, without loss, at the end of the process. The sulphurous has derived the oxygen necessary to convert it into sulphuric acid, really from the air, but in an indirect manner.

In the manufacture upon the large scale, the sulphurous acid is converted into sulphuric acid, in oblong chambers of sheet-lead, supported by an external framework of wood. Sulphurous acid from burning sulphur, nitric acid vapour, and steam, are simultaneously admitted into the leaden chamber; and the sulphuric acid formed accumulates in the liquid state upon the floor of the chamber. The diagram below represents one of the forms of the chamber, with its appendages.

FIG. 139.



a represents the water boiler with its furnace, for supplying the chamber with steam; *b*, the section of a small chamber in brickwork, or furnace, called the burner, upon the floor of which the sulphur burns, and in which there is a tripod supporting an iron capsule, which contains the materials for nitric acid, namely, oil of vitriol, and either nitre or nitrate of soda. The heat of the burning sulphur evolves the nitric acid from these materials, and consequently the sulphurous acid becomes mixed with nitric acid vapour, which it carries forward with it, by a tube represented in the figure, into the chamber, where these acid vapours meet with the steam admitted near the same point, and the formation of sulphuric acid takes place. The nitric acid vapour is equivalent to binoxide or to peroxide of nitrogen, as the first effect of the sulphurous acid is to reduce the nitric acid to a lower state of oxidation. From 8 to 19 parts of sulphur are consumed in the burner for 1 part of nitrate of soda decomposed there, so that the quantity of nitrous fumes is small compared with the quantity of sulphurous acid thrown into the chamber. The chamber represented is 72 feet in length by 14 in breadth, and 10 in height, and is divided into three compartments, by leaden curtains placed across it, two of which, *d* and *f*, are suspended from the roof, and reach to within six inches of the floor, and one, *e*, rises from the floor to within six inches of the roof: *g* is a leaden conduit tube, for the discharge of the uncondensible gases, which should communicate with a tall chimney, to carry off these gases and to occasion a slight draught through the chamber. The curtains serve to detain the vapours, and cause them to advance in a gradual manner through the chamber, so that the sulphuric acid is deposited as completely as possible, before the vapours reach the discharge tube. When the oxygen of the chamber is exhausted, the admission of acid vapours is discontinued, till the air in it is renewed. But the admission of air to the chamber is generally so regulated, that a continuous current is maintained through the chamber, and the combustion proceeds without interruption. When steam is admitted in proper quantity, as in this method, it is not necessary to begin by covering the floor with water.

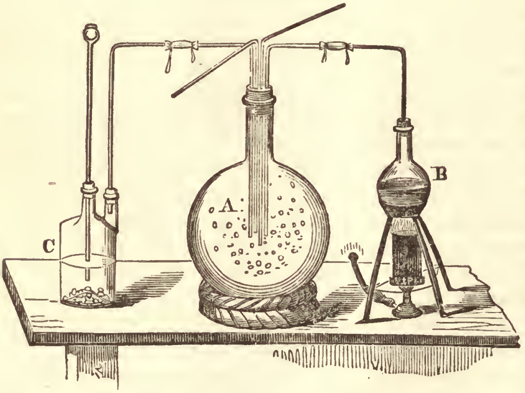
The acid may be drawn off from the floor of the chamber of a sp. gr. as high as 1.6. It is further concentrated in open leaden pans, till it begins to act upon the metal, and afterwards in retorts of platinum or glass. It still retains small quantities of nitrous acid and sulphate of lead, from which it can be completely purified by dilution with water and a second distillation. The acid thus obtained, in its most concentrated state, is a definite compound of one eq. acid and one eq. of water, $HO.SO_3$, which last cannot be separated by heat, the hydrate distilling over unchanged. It is the Oil of Vitriol of commerce.

The construction of the leaden chamber is greatly varied; one chamber of great dimensions is often used without any division by curtains; or the vapour is carried successively through a series of three, four, or five connected chambers. The sulphurous acid, also, is often derived from the combustion of bisulphide of iron (iron pyrites), instead of sulphur; a peculiar kiln or flue being employed for burning the former. At the suggestion of Gay-Lussac, the nitrous vapour, as it ultimately leaves the chamber with the air exhausted of oxygen, is absorbed by being made to pass through a column of coke, over which a stream of the concentrated sulphuric acid is flowing. The sulphuric acid, after being charged with nitrous vapours or nitric acid, is transported back to the anterior part of the chamber, and there exposed to the sulphurous acid, as the latter leaves the sulphur burner. This exposure *denitrates* the sulphuric acid, much sulphurous acid becoming sulphuric acid, and peroxide of nitrogen being liberated in the state of vapour. (See Knapp's Chemical Technology, edited by Drs. Ronalds and Richardson, i. 234, Am. ed.).

When the supply of aqueous vapour in the chamber is insufficient, a white crystalline compound appears, known as the crystalline substance of the leaden chambers: it is deposited most frequently in the tube by which two chambers communicate. It contains the elements of 2 eq. sulphuric acid, and 1 eq. nitric acid, $2SO_2+NO_5$; but several other views of the arrangement of its elements may be entertained with equal probability. This substance, which is also termed azoto-sulphuric acid (S_2NO_9), is decomposed by water, and gives sulphuric acid, nitric acid, and binoxide of nitrogen:

$$3(S_2NO_9) \text{ and } 7HO=6(HO.SO_3) \text{ and } HO.NO_5, \text{ and } 2NO_2.$$

FIG. 140.



The formation of the crystalline substance, and the general operation of the leaden chamber, may be illustrated by the arrangement in fig. 140. Binoxide of nitrogen evolved by the action of dilute nitric acid on copper in the gas-bottle C, and sulphurous acid evolved by the action of copper clippings on concentrated sulphuric acid in the flask B, are conveyed into a large glass globe, A, containing air. Ruddy fumes of peroxide of nitrogen first appear, but soon the inner surface of the globe is frosted over with the crystalline compound. If steam or water be now introduced, by one of the free tubes, the crystals disappear with effervescence, from escape of gas, sulphuric acid is produced, and the changes are repeated till the air in A is exhausted.

Properties.—Anhydrous sulphuric acid is obtained by gently heating the fuming acid of Nordhausen in a retort, and receiving its vapour in a bottle artificially cooled, which can afterwards be closed by a glass stopper. It condenses in solid fibres, like asbestos, which are tenacious, and may be moulded by the fingers like wax. The density of the solid at 68° is 1.97: at 77° it is liquid; and a little above that temperature it enters into ebullition, affording a colourless vapour, which produces dense white fumes on mixing with air, by condensing moisture. The dry acid does not redden litmus, an effect which requires the presence of moisture. It combines with sulphur, and produces liquid compounds, which are of a brown, green, and blue colour, and, with one-tenth of its weight of iodine, forms a compound of a fine green colour, which assumes the crystalline form. Heated in the acid vapour, caustic lime or baryta inflames and burns for a few seconds; the vapour is absorbed, and sulphate of lime or baryta formed. The anhydrous acid has a great affinity for water, and when dropped into that liquid, occasions a burst of vapour from the heat evolved. The density of its vapour was found to be 3000 by Mitscherlich, but it is probably 2762, and formed of 3 volumes of oxygen and 1 volume of sulphur vapour condensed into 2 volumes, which constitute its combining measure. This vapour is resolved by a strong red heat into sulphurous acid and oxygen.*

When the Nordhausen acid is retained below 32°, well-formed crystals appear in it, which Mitscherlich finds to be a compound of two equivalents of acid and one of water, or $2SO_3 + HO$. (Elémens de Chimie, par E. Mitscherlich, t. ii. p. 57). This compound is resolved by heat into the anhydrous acid, which sublimes, and the first hydrate, or oil of vitriol.

The most concentrated oil of vitriol of the leaden chambers ($HO + SO_3$) is a dense, colourless fluid of an oily consistence, which boils at 620°, and freezes at —29°, yielding often regular six-sided prisms of a tabular form. It has a specific gravity at 60° of 1.845. It is a most powerful acid, supplanting all others from their combinations, with a few exceptions, and when undiluted is highly corrosive. It chars and destroys most organic substances. It has a strong sour taste, and reddens litmus even though greatly diluted. Sulphur is soluble to a small extent in the concentrated acid, and communicates a blue, green, or brown tint to it; so are selenium and tellurium. Charcoal also appears to be slightly soluble in this acid, imparting to it a pink tint, which afterwards becomes reddish-brown. The concentrated acid has a great affinity for water, which it absorbs from the atmosphere, and is usefully employed to dry substances placed near it in vacuo. Considerable heat is evolved in its combination with water: when 4 parts by weight of the concentrated acid are suddenly mixed with 1 part of water, the temperature rises to 300°. When diluted with about thirty times its weight of water, sulphate of water $HO.SO_3$, evolves heat, which may be represented by 23 degrees; while $HO.SO_3 + HO$, similarly diluted, evolves 14 degrees, or 9 degrees less, and $HO.SO_3 + 5HO$, 5 degrees only, or 18 degrees less. Hence the first equivalent of water which combines with oil of vitriol appears to evolve as much heat as the following four equivalents (Mem. Chem. Soc., i. 107). In a series of valuable experiments by M. Abria, but which do not admit of being compared with the preceding, he obtained the following results (Annales de Ch. et Ph., 3 sér., xii. 171):—

Quantities of heat disengaged by the combination of sulphate of water,—

With 1 eq. water	64.25	degrees.
2 "	94.69	"
3 "	113.06	"
4 "	124.43	"
5 "	131.66	"
Excess	165.63	"

The anhydrous acid SO_3 disengaged 237.13 degrees in combining with an excess of water. The value of these last degrees, or the unit of heat, is the quantity of heat required to heat up 1 gramme (15.434 grs.) of water 1° Centigrade. Abria concludes that in the combination of anhydrous sulphuric acid with water, the quantities of heat successively disengaged by the different equivalents of water have a multiple relation, and correspond very closely, for the first equivalents, with the numbers—

$$1,\ \tfrac{1}{3},\ \tfrac{1}{6},\ \tfrac{1}{12},\ \tfrac{1}{16},\ \tfrac{1}{24}.$$

The density of sulphuric acid becomes always less by dilution, but not exactly in the ratio of the water added. (Table of Densities of Sulphuric Acid, in Appendix).

Acid of density 1.78 is the second definite hydrate, containing two eq. of water to one of acid. This hydrate forms large and regular crystals, even a little above the freezing point of water, and was observed by Mr. Keir to remain solid till the

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* [*See Supplement*, p. 781.]

temperature rose to 45°. If the dilute acid is evaporated at a heat not exceeding 400°, its water is reduced to the proportion of this hydrate. This second eq. of water is expelled by a higher temperature, but the first eq. can only be separated from the acid by a stronger base. Sulphuric acid forms still a third hydrate, of sp gr. 1.632, containing three eq. of water, the proportion to which the water of a more dilute acid is reduced, by evaporation in vacuo at 212°. It is also in the proportions of this hydrate that the acid and water undergo the greatest condensation, or reduction of volume, in combining. The following, then, are the formulæ of the definite hydrates of this acid, including that derived by Mitscherlich from the Nordhausen acid :—

HYDRATES OF SULPHURIC ACID.

Hydrate in the Nordhausen acid	$HO.2SO_3$
Oil of vitriol, (sp. gr. 1.845)	$HO.SO_3$
Acid of sp. gr. 1.78	$HO.SO_3+HO$
Acid of sp. gr. 1.632	$HO.SO_3+2HO$

The composition of a hydrate of sulphuric acid is ascertained by adding a known weight of oxide of lead to the liquid, in a capsule, and evaporating to dryness. As the sulphuric acid abandons all its water on combining with oxide of lead, and the sulphate of lead may be heated without decomposition, the increase of weight which the oxide on the capsule undergoes is precisely the quantity of dry sulphuric acid in the hydrate examined.

Sulphuric acid acts in two different modes upon metals, dissolving some, such as copper and mercury, with the evolution of sulphurous acid, and others, such as zinc and iron, with the evolution of hydrogen gas. The metal is oxidated at the expense of the acid itself in the one case, and of the water in combination with the acid in the other. The acid acts with most advantage in the first mode when concentrated, and in the second when considerably diluted.

The presence of sulphuric acid in a liquid may always be discovered by means of chloride of barium, which produces with this acid a white precipitate of sulphate of baryta, insoluble in both acids and alkalies.

Sulphates.—Of no class of salts do chemists possess a more minute knowledge than of the sulphates. The sulphates of zinc, magnesia, and other members of the magnesian family, correspond closely with the hydrate of sulphuric acid. Thus of the seven eq. of water which the crystallized sulphate of magnesia possesses, it retains one at 400°, and is then analogous to the sulphate of water of sp. gr. 1.78; the formula of these two salts being,

$$MgO.SO_3+HO,$$
$$HO.SO_3+HO,$$

and the eq. of water in both salts may be replaced by sulphate of potassa, when the sulphate of water forms the salt called the bisulphate of potassa, and the sulphate of magnesia forms the double sulphate of magnesia and potassa, of which the formulæ also correspond:—

$$HO.SO_3+KO.SO_3$$
$$MgO.SO_3+KO.SO_3.$$

In all these sulphates there is one eq. of acid to one of base; but with potassa, sulphuric acid is supposed to form a second salt, in which two of acid are combined with one of base $KO+2SO_3$, and which is said to have lately been obtained in a crystallized state by M. Jacquelin (Annal. de Chim. et de Phys., lxx. 311). This would be a true bisulphate, and would correspond to the red chromate or bichromate of potassa $KO+2CrO_3$; but my own observations have obliged me to call in question the existence of this anhydrous bisulphate (Mem. Chem. Soc., i. 120).

Uses.—Sulphuric acid is employed to a large extent in eliminating nitric acid from nitrate of potassa, and in the preparation of hydrochloric acid and chlorine from chloride of sodium, and also in the processes of bleaching. But the great consumption of this acid is in the formation of sulphates, particularly of sulphate of soda, nearly all the carbonate of soda of commerce being at present procured by the decomposition of that salt.

CHLOROSULPHURIC ACID.

Eq. 67.5 *or* 843.75; SO_2Cl; *density* 4652 ◫

Sulphurous acid gas combines with an equal volume of chlorine under the influence of light, and condenses into oily drops, which are denser than water (Regnault, Annales de Chim. et de Phys. lxix. 170, and lxxi. 445). Chlorosulphuric acid in dissolving decomposes 1 eq. of water, and is converted into hydrochloric acid and sulphuric acid,—a reaction which demonstrates the original compound to consist of 1 eq. of sulphurous acid with 1 eq. of chlorine.

The density of the vapour of chlorosulphuric acid was found by experiment to be 4703, which agrees with the theoretical density, 4652. It consists of 2 volumes of sulphurous acid and 2 volumes of chlorine condensed into 2 volumes, which form the combining measure of the vapour. In its condensation, it resembles the vapour of anhydrous sulphuric acid. This body also corresponds exactly in composition with the compound hitherto called chlorochromic acid; CrO_2Cl, chromium being substituted in the latter for the sulphur of the former.

With dry ammoniacal gas, chlorosulphuric acid forms a white powder, which is a mixture of the hydrochlorate of ammonia (sal ammoniac) and *sulphamide*, SO_2+NH_2. It does not combine, as an acid, with bases.

Chlorosulphuric acid may also be represented as a compound of sulphuric acid with a terchloride of sulphur, $3SO_3+SCl_3$. Another compound of the same series has been formed by H. Rose, which is represented by $5SO_3+SCl_3$.

NITROSULPHURIC ACID.

Eq. 62 *or* 775; SNO_4 *or* $SO_2.NO_2$; *not isolable.*

Sir H. Davy made the observation that binoxide of nitrogen is absorbed by a mixture of sulphite of soda and caustic soda, and that a compound is produced, of which the principal characteristic is to disengage abundance of protoxide of nitrogen, upon the addition of an acid to it. He concluded that the nitrous oxide, which then escapes, was previously united with soda, and gave this as an instance of the combination of that neutral oxide with an alkali. As the sulphite of soda became at the same time sulphate, the conversion of the nitric oxide into nitrous oxide appeared to be explained. It was afterwards shown by Pelouze that a new acid is formed in the circumstances of the experiment, to which he has given the name nitrosulphuric, and which may be considered as a compound of sulphurous acid and nitric oxide, or another member of the sulphurous acid series. (Pelouze, in Taylor's Scien. Mem., vol. i. p. 470; or Annal. de Chim. et de Phys. lx. 151).

Preparation.—If a mixture be made over mercury of 2 volumes of sulphurous acid, and 4 volumes of binoxide of nitrogen, which are combining measures of these gases, no change occurs; but on throwing up a strong solution of caustic potassa into the gases, they disappear entirely after some hours, combining with a single equivalent of potassa, and forming together the nitrosulphate of potassa. But it is better to prepare the nitrosulphate of ammonia. A concentrated solution is made of sulphite of ammonia, which is mixed with five or six times its volume of solution of ammonia, and into this binoxide of nitrogen is passed for several hours at a low temperature. A number of beautiful crystals are gradually deposited; they are to be washed with a solution of ammonia, previously cooled, which, besides the advantage of retarding their decomposition, offers that of dissolving less of them than pure water. When the crystals are desiccated, they should be introduced into a well-closed bottle; in this state they undergo no alteration. The same process is applicable to the corresponding salts of potassa and soda. When a strong acid is added to a solution of these salts, for the purpose of liberating the nitrosulphuric acid, the latter, on being set free, decomposes spontaneously into sulphuric acid and protoxide of nitrogen, which comes off with effervescence.

Properties. — The acid of the nitrosulphates is not precipitated by baryta. The nitrosulphate of potassa, when heated, becomes sulphite, and evolves nitric oxide; but the salts of soda and ammonia become sulphates, and evolve nitrous oxide. No nitrosulphates of the metallic oxides, which are insoluble in water, have been formed, or appear capable of existing; for when such salts as chloride of mercury, sulphate of zinc or of copper, sulphate of sesquioxide of iron and nitrate of silver, are added to the nitrosulphate of ammonia, they produce a brisk effervescence of nitrous oxide, with the formation of sulphate of ammonia, or they decompose the nitrosulphate of ammonia as free acids do. Indeed, the only nitrosulphates which have been formed are those of potassa, soda, and ammonia. These are neutral, and have a sharp and slightly bitter taste, with nothing of that of the sulphites.

These salts rival the binoxide of hydrogen in facility of decomposition. The nitrosulphate of ammonia resists 230°, but is decomposed with explosion a few degrees above that temperature, caused by the rapid disengagement of nitrous oxide. Solutions of the nitrosulphates are not stable above the freezing point, but their stability is much increased by an excess of alkali. They are resolved into sulphate and nitrous oxide, by the mere contact of certain substances which do not themselves undergo any change; such as spongy platinum, silver and its oxide, charcoal powder and binoxide of manganese, by acids, even carbonic acids, and by metallic salts.

Azoto-sulphuric acid of De la Provostaye, S_2NO_9.—Liquid sulphurous acid and peroxide of nitrogen, sealed up together in a glass tube, react upon each other, and give rise to a solid compound crystallizing in rectangular square prisms, which has been examined by M. de la Provostaye. A small portion of a blue liquid, possessing an explosive property, which has not been fully examined, is formed at the same time. This substance forms the "crystals of the leaden chamber." It may also be produced, according to Gay-Lussac, by bringing peroxide of nitrogen and oil of vitriol in contact:—

$$2NO_4 \text{ and } 2(HO.SO_3) = HO.NO_5 + HO \text{ and } S_2NO_9.$$

This substance fuses at about 430°, and forms a silky mass on cooling; it may be distilled without decomposition at about 620°. It is decomposed by water, sulphuric acid being formed, and nitrous vapours disengaged. It has been represented as composed of $2SO_2+NO_5$; or as $2SO_3+NO_3$; or $S_2O_5+NO_4$; but nothing certain is known of its molecular arrangement.

Dry binoxide of nitrogen is absorbed by anhydrous sulphuric acid, according to an observation of H. Rose.

HYPOSULPHURIC ACID.

Eq. 72 *or* 900; S_2O_5; *not isolable.*

Preparation. — This acid of sulphur was discovered by Gay-Lussac and Welter, in 1819. To prepare it, a quantity of binoxide of manganese, which must not be hydrated, is reduced to an extremely fine powder, suspended by agitation in water, and sulphurous acid gas is transmitted through the water. When ordinary binoxide of manganese is used, it should be previously treated with nitric acid, to dissolve out the hydrated oxide, and washed. The temperature is apt to rise during the absorption of the gas, but must be repressed, otherwise much sulphuric acid is produced, — the formation of which, indeed, it is impossible to prevent entirely, but of which the quantity is said to be reduced almost to nothing, when the liquid is kept cold during the operation. The binoxide of manganese disappears, and a solution of hyposulphate of the protoxide of manganese is formed; 2 equivalents of sulphurous acid, and 1 of binoxide of manganese, forming one of hydrosulphuric acid and one of protoxide of manganese, or

$$2SO_2 \text{ and } MnO_2 = MnO + S_2O_5.$$

The solution is filtered, and then mixed with a solution of sulphide of barium, which occasions the precipitation of the insoluble sulphide of manganese, with the transference of the hyposulphuric acid to baryta. From this hyposulphate of baryta, the hyposulphates of other metallic oxides may be prepared by adding their sulphates to that salt, when the insoluble sulphate of baryta will precipitate, and the hyposulphate of the metallic oxide added remain in solution. But to procure the hyposulphuric acid itself, the solution of hyposulphate of baryta may be evaporated to dryness, and, being perfectly pure, it is reduced to a fine powder, weighed, and dissolved in water: for 100 parts of it 18.78 parts of oil of vitriol are taken, which, after dilution with three or four times as much water, are employed to decompose this salt of baryta. The liberated hyposulphuric acid solution is filtered, and evaporated *in vacuo* over sulphuric acid, till it attains a density of 1.347, which must not be exceeded, as the acid solution begins then to decompose spontaneously into sulphurous acid, which escapes, and sulphuric acid, which remains in the liquid.

Properties. — This acid has not been obtained in the anhydrous condition. Its aqueous solution has no great stability, being decomposed at its temperature of ebullition. The same solution exposed to air in the cold, slowly absorbs oxygen, according to Heeren, and becomes sulphuric acid. But neither nitric acid, nor chlorine, nor binoxide of manganese, oxidize this acid unless they are boiled in its solution. Its salts are perfectly stable, either when in solution or when dry, and are generally very soluble, having some analogy to the nitrates. A hyposulphite, when heated to redness, leaves a neutral sulphate, and allows a quantity of sulphurous acid to escape, which would be sufficient to form a neutral sulphite with the base of the sulphate. This class of salts was particularly examined by Heeren (Poggendorff's Annalen, v. vii. p. 77). Hyposulphuric acid is imagined to exist in acid compounds produced by the action of sulphuric acid on several organic substances.

The hyposulphate of baryta may be analysed by exposing a portion of it to a red heat, when it gives off sulphurous acid, and leaves pure sulphate of baryta behind. If an equal portion be treated with boiling concentrated nitric acid, the sulphurous acid is converted into sulphuric acid; and if chloride of barium is afterwards added, a quantity of sulphate of baryta is obtained which is exactly double in weight that obtained from the first portion.

HYPOSULPHUROUS ACID.

Eq. 48 *or* 600; S_2O_2, *or* $SO_2 + S$; *not isolable.*

The hyposulphites are better known than hyposulphurous acid itself, which is a body of little stability, quickly undergoing decomposition when liberated by a stronger acid from a solution of any of its salts, and resolving itself into sulphurous acid, hydrosulphuric acid, and sulphur. These salts, long considered as a species of double salts, and called ***sulphuretted sulphites***, were first supposed to contain a peculiar acid by Dr. T. Thomson and by Gay-Lussac, — a conjecture afterwards verified by Sir John Herschel, whose early researches upon this acid form the subject of an interesting memoir (Ed. Phil. Journ. vol. i. pp. 8 and 396).

Preparation. — Sulphide of soda is prepared, in the first instance, by saturating a solution of carbonate of soda with sulphurous acid gas, by the apparatus described at page 294). This sulphite, care being taken that it is not acid, is converted into hyposulphite, by digesting it upon flowers of sulphur at a high temperature, but without ebullition. The sulphurous acid assumes 1 eq. of sulphur, and remains in combination with the soda; or, in symbols —

$$NaO + SO_2 \text{ and } S = NaO + SO_2.S.$$

The solution may afterwards be evaporated (ebullition being always avoided, as the hyposulphites are partially decomposed at 212°), and affords large crystals of the hyposulphite of soda. When solution of caustic soda is digested upon sulphur, the latter is likewise dissolved, and a mixture of 1 eq. of hyposulphite of soda with 2 eq. of sulphide of sodium results, of which the last always dissolves an excess of sulphur: —

$$3NaO \text{ and } 4S = NaO + S_2O_2 \text{ and } 2NaS.$$

Exposed to the air, this solution slowly absorbs oxygen, and if it contains a certain excess of sulphur, passes entirely into hyposulphite of soda.

The hyposulphite of lime is also formed by digesting together 1 part of sulphur and 3 of hydrate of lime at a high temperature, when changes of the same nature occur as with sulphur and caustic soda, and the solution becomes red, containing bisulphide of calcium: a stream of sulphurous acid gas is conducted through the solution after it has cooled, and converts the whole salt into hyposulphite, occasioning at the same time a considerable deposition of sulphur. The reaction here may be expressed by the following formula: —

$$2CaS_2 \text{ and } 3SO_2 = 2CaO + 2S_2O_2 \text{ and } 3S.$$

If the waste-lime, in the porous state in which it is removed from the dry-lime purifiers of a gas-work, be exposed to air, it rapidly absorbs oxygen; and, when treated with water, afterwards gives much soluble hyposulphite of lime. This is an economical method of preparing the salt on a large scale (Mem. Chem. Soc. ii. 358).

Zinc and iron also dissolve in the solution of sulphurous acid in water, with little or no effervescence, deriving the oxygen necessary to convert them into oxides, not from water, but from the sulphurous acid, two-thirds of which are thereby converted into hyposulphurous acid, which combines with half the oxide produced; while the other third, remaining as sulphurous acid, unites with the other moiety of the same oxide: —

$$3SO_2 \text{ and } 2Zn = ZnO.S_2O_2 \text{ and } ZnO.SO_2.$$

The hyposulphite obtained by this process is, therefore, mixed with a sulphite.

Properties. — The acid of these salts undergoes decomposition when they are strongly heated, or treated with an acid. It forms soluble salts with lime and strontia, in which respect it differs from sulphurous and sulphuric acids; the hyposulphite of baryta is insoluble. It also forms a remarkable salt with silver, which has no metallic flavour, but tastes extremely sweet. The existence of a hyposulphite in a solution is easily recognised, by its possessing the power to dissolve freshly precipitated chloride of silver, and become sweet. Hyposulphite of soda in solution is apt to become acid by the absorption of oxygen, and then its conversion into sulphate of soda, with deposition of sulphur, proceeds rapidly.

Uses. — The hyposulphite of soda is employed to distinguish between the earths strontia and baryta, — the latter of which it precipitates, and not the former. It is also applied, in certain circumstances, to dissolve the insoluble salts of silver in photography, electro-plating, and the treatment of silver ores.

POLYTHIONIC SERIES.

Three new acids of sulphur have lately been discovered, all containing, like hyposulphuric acid, 5 eq. of oxygen, but evidently more related in constitution and properties to hyposulphurous acid. They were named by Berzelius, from Θειον (sulphur); and are composed as follows:—

Trithionic, or monosul-hyposulphuric acid	S_3O_5, *or* $S_2O_5 + S$
Tetrathionic, or bisul-hyposulphuric acid	S_4O_5, *or* $S_2O_5 + 2S$.
Pentathionic, or trisul-hyposulphuric acid	S_5O_5, *or* $S_2O_5 + 3S$.

Hyposulphurous acid becomes the dithionous, and hyposulphuric acid the dithionic acid, as members of the same series; all of which, it will be observed, contain more than 1 equivalent of sulphur, and are therefore polythionic: but the old names of the two acids last referred to are too firmly established to be changed, without a greater necessity for the alteration than appears to exist.

Trithionic or *Monosul-hyposulphuric acid;* eq. 88 *or* 1100, S_3O_5 *or* S_2O_5+S.—This acid was first obtained by M. Langlois (Annal. de Chim. 3 ser. iv. 77). It is the result of the action of sulphur upon the soluble bisulphites, and may be prepared from the bisulphite of baryta. This salt is digested with flowers of sulphur at a temperature not exceeding 122° (50° C.) for several days; the solution first becomes yellow, afterwards loses all colour, and when allowed to cool in this state, deposits a salt in long white silky crystals, which is the trithionate of baryta. By the cautious addition of sulphuric acid to a solution of the new salt, the trithionic acid may be liberated and obtained in solution, while the insoluble sulphate of baryta precipitates. The acid solution may be concentrated in the vacuous receiver of an air-pump, but is rapidly decomposed by heat into sulphurous acid and sulphur. The salt of potassa is easily obtained, either, according to Plessy's method, by passing sulphurous acid into a solution of hyposulphite of potassa; or, according to Langlois, into one of sulphide of potassium: in the latter case hyposulphite of potassa is first formed, and from that the trithionate. (Kessner, Chem. Gaz. vi. p. 369.) The salts of this acid appear to have greater stability than the hyposulphites, and are formed when certain hyposulphites, such as those of zinc, cadmium, and lead, are left to spontaneous decomposition; or even, according to Fordos and Gelis, by the sole effect of the concentration of solutions of these salts. This acid is precipitated black by the salts of the suboxide of mercury, a property which distinguishes the trithionic acid from the two more highly sulphured acids of the same series, which are precipitated yellow by the reagent in question.

Tetrathionic or *Bisul-hyposulphuric acid;* eq. 104 *or* 1300; S_4O_5 *or* $S_2O_5+S_2$.—This acid was discovered by MM. Fordos and Gelis, and is obtained by dissolving iodine in a solution of the hyposulphites, particularly of the hyposulphite of baryta. The reaction in the last case is as follows:—

$$2\ (BaO.S_2O_2) \text{ and } I = BaI \text{ and } BaO.S_4O_5.$$

The new salt, being less soluble than the iodide of barium, is separated by crystallization, and affords the acid when decomposed by a suitable proportion of sulphuric acid. The solution of tetrathionic acid has considerable stability, and may be highly concentrated. The process just described is modified by Kessner, who prepares first the hyposulphite of lead by dissolving 2 parts of hyposulphite of soda in hot water, and pouring this solution into an equally hot dilute solution of 3 parts of acetate of lead. The precipitate is washed with a large quantity of warm water, and mixed (still moist) with 1 part of iodine, and the mass frequently stirred; in the course of a few days the whole is converted into iodide of lead and a solution of tetrathionate of lead. The lead is now removed by sulphuric acid (the use of hydrosulphuric acid being inadmissible), any excess of the latter by carbonate of baryta, and the solution of the tetrathionic acid evaporated. When this acid is saturated with carbonate of soda, or its salt of lead decomposed by sulphate of soda, only products of decomposition are obtained,—sulphur, sulphate, and hyposulphite of soda. (Chem. Gaz. vi., p. 370.) The salts of this acid, therefore, require to be prepared directly, and appear generally to be less stable than the hydrated acid.

Pentathionic or *Trisul-hyposulphuric acid;* = 120 *or* 1500; S_5O_5 *or* $S_2O_5+S_3$.—Several years ago Dr. T. Thomson observed that when hydrosulphuric and sulphurous acids mutually decompose each other in presence of water, the magma of sulphur precipitated is impregnated by a peculiar acid. M. Wackenroder lately found that this acid is an additional number of the present series. To prepare the acid, Wackenroder supersaturates water with sulphurous acid, and then causes hydrosulphuric acid to stream through it till the liquid has the odour and reactions of the latter, evaporating afterwards till the excess of hydrosulphuric acid is expelled. The liquid does not become clear till after clean slips of copper are left in it for some time, to remove the suspended sulphur: copper reduced from the oxide by hydrogen would probably act more rapidly. The addition of chloride of sodium, or saturation with a base, such as an alkaline carbonate, also facilitates the precipitation of the sulphur. In the opinion of Mr. L. Thompson, much of this sulphur, which is supposed to be suspended, is actually in solution.

The clear acid liquid may be concentrated till it attains a density of 1.37; it is inodorous, sour, and a little bitter. It may be preserved at the temperature of the air, without change; but when made to boil it undergoes decomposition, giving off hydrosulphuric acid, followed by sulphurous acid, and leaving behind ordinary sulphuric acid and some sulphur. This acid is decomposed, like the last, by strong bases.

Pentathionic acid was also found by Fordos and Gelis among the products of the decomposition of the chlorides of sulphur by water. The pentothionate of baryta is very soluble, and is easily altered. It was analysed by means of chlorine and the hypochlorites, which transform the whole sulphur into sulphuric acid:

$$S_5O_5 \text{ and } 10\ Cl \text{ and } 10\ HO = 5\ SO_3 \text{ and } 10\ HCl.$$

The pentathionic acid is distinguished from hyposulphurous acid, with which it is isomeric, by the less solubility of the pentathionates, and by the circumstance that the pentathionates have no action upon iodine (Annales de Ch. 3. ser. xxii. 66). The sulphur was supposed by Berzelius to exist in the various polythionic acids, in its different allatropic conditions.

SULPHUR AND HYDROGEN.

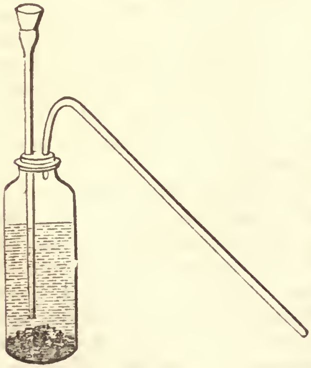
HYDROSULPHURIC ACID.

Syn. Sulphuretted hydrogen gas, sulfhydric acid; Eq. 17 *or* 212.5; SH; *density* 1191.2; □□

Sulphur does not combine directly with hydrogen even when heated in that gas, but with that element, notwithstanding, sulphur forms at least two compounds; one of which, hydrosulphuric acid, is a reagent of frequent application and considerable importance.

Preparation.—(1.) Of those metals which dissolve in dilute sulphuric acid, with the displacement of hydrogen, the protosulphides dissolve also in the same acid, but the hydrogen then evolved carries off sulphur in combination, and appears as hydrosulphuric acid gas. The protosulphide of iron, which is commonly employed in this operation, is obtained by depriving yellow pyrites, or bisulphide of iron, of a portion of its sulphur by ignition in a covered crucible; or formed directly by exposing to a low red heat a mixture of 4 parts of coarse sulphur and 7 of iron filings or borings in a covered stoneware or cast-iron crucible. The sulphide of iron, thus obtained, is broken into lumps, and acted upon by diluted sulphuric acid in a gas-bottle (fig. 141), exactly as zinc is treated in the preparation of hydrogen gas. Hydrosulphuric acid is evolved without the application of heat, and should be collected over water at 80° or 90°; or if collected in a gasometer or gasholder, the latter may be filled with brine, in which this gas is less soluble than in pure water. The gas obtained by this process generally contains free hydrogen, arising from an intermixture of metallic iron with the sulphide of iron used. The gas may also be evolved from the action of hydrochloric acid upon the sulphide of iron, but as it is then impregnated with the vapour of the

FIG. 141.

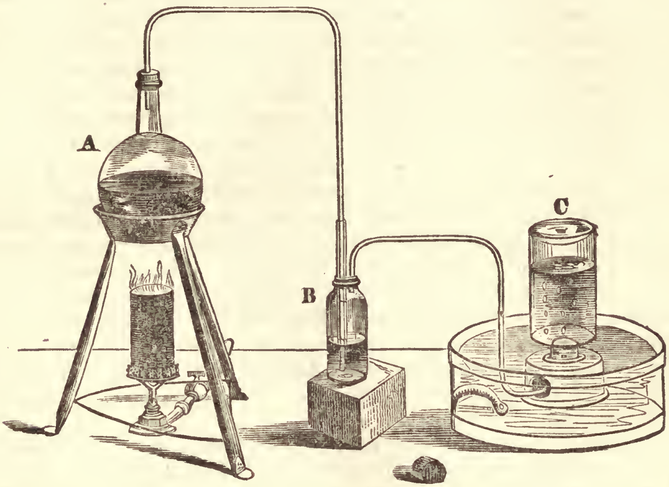


latter acid, and may also, like every gas produced with effervescence, carry over drops of fluid, it should always be transmitted through water in a wash-bottle, before being applied to any purpose as pure gas. The reaction by which hydro-sulphuric acid is usually evolved is expressed in the following equation:

$$\text{FeS and HO.}\dot{\text{S}}\text{O}_3 = \text{HS and FeO.SO}_3.$$

(2.) Hydrosulphuric acid, without any admixture of free hydrogen, is obtained by digesting in a flask A, used as a retort (fig. 142), with a gentle heat, sulphide of antimony in fine powder with concentrated hydrochloric acid, in the proportion of 1 ounce of the former to 4 ounce measures of the latter. The gas of this operation is passed through water in a wash-bottle B, and collected over water at 80°, in a bottle C, provided with a good cork. Or, after passing through the wash-bottle, it may be carried over chloride of calcium in a drying tube, and collected over mercury, but is gradually decomposed by that metal, which has a strong affinity for sulphur, and hydrogen is liberated, without any change of volume. The reaction between hydrochloric acid and sulphide of antimony may be thus expressed:

FIG. 142.



$$\text{3HCl and SbS}_3 = \dot{3}\text{HS and SbCl}_3.$$

Properties.—Hydrosulphuric acid is a colourless gas, of a strong and very nauseous odour. Its density is 1191.2, by the experiments of Gay-Lussac and Thenard, and its theoretical sp. gr. 17 times that of hydrogen. It consists of 2 volumes of hydrogen and 1 volume of sulphur vapour, condensed into 2 volumes, which form its combining measure. Hydrosulphuric acid is partially decomposed by heat into hydrogen and sulphur; but to obtain complete decomposition it is necessary to pass the gas a great many times through a porcelain tube placed across a furnace, and strongly heated. By a pressure of 17 atmospheres at 50°, it is condensed into a highly limpid colourless liquid, of sp. gr. 0.9, which is of peculiar interest as the analogue of water in the sulphur series of compounds: the solvent powers of this liquid have not been examined. When cooled to —122°, it solidifies, and is then a white crystalline translucent substance, heavier than the liquid (Faraday). The air of a chamber slightly impregnated by this gas may be respired without injury, but a small quantity of the undiluted gas inspired occasions syncope, and its respiration, in a very moderate proportion, was found by Thenard to prove fatal, —birds perishing in air containing 1-1500th, and a dog in air containing 1-800th part of this gas. Its poisonous effects are best counteracted by a slight inhalation of chlorine gas, as the latter may be obtained from a little chloride of lime placed in the folds of a towel wetted with acetic acid. Water dissolves, at 64°, 2½ volumes of this gas, and alcohol 6 volumes. These solutions soon become milky when exposed to air, the oxygen of which combines with the hydrogen of the gas and precipitates the sulphur. Those mineral waters termed sulphureous, such as Harrowgate, contain this gas, although rarely in a proportion exceeding 1½ per cent. of their volume. They are easily recognized by their odour and by blackening silver. It is also found in foul sewers and in putrid eggs. Of deodourizing fluids the solution of nitrate of lead, chloride of zinc, sulphate of iron, and sulphate of manganese, appear to be equally efficacious; the first alone decomposing the free gas, but that salt, and all the others named, decomposing hydrosulphuric acid when in combination with ammonia, the form in which it usually emanates from putrefactive matter.

Hydrosulphuric acid is highly combustible, and burns with a pale blue flame, producing water and sulphurous acid, and generally a deposit of sulphur when oxygen is not present in excess. A little strong nitric acid thrown into a bottle of this gas, occasions the immediate oxidation of its hydrogen, and often a slight explosion with flame, when the escape of the vapour is impeded by closing the mouth of the bottle. Hydrosulphuric acid is immediately decomposed by chlorine, bromine, and iodine, which assume its hydrogen: hence the odour of this gas in a room is soon destroyed on diffusing a little chlorine through it. Tin, and many other metals, heated in this gas, combine with its sulphur with flame, and liberate an equal volume of hydrogen, affording ready means of demonstrating the composition of the gas. Potassium decomposes one half of the gas in that manner, and becomes sulphide of potassium, which unites with the other half without decomposition, forming the hydrosulphate of the sulphide of potassium. The action of other alkaline metals upon hydrosulphuric acid is similar.

This compound has a weak acid reaction, and forms one of the hydrogen-acids. It does not combine and form salts with basic oxides, but it unites with basic sulphides, such as sulphide of potassium, and forms compounds which are strictly comparable with hydrated oxides. When hydrosulphuric acid is passed over lime at a red heat, both compounds are decomposed, and water with sulphide of calcium is formed. The oxides of nearly all the metallic salts, whether dry or in a state of solution, are decomposed by hydrosulphuric acid in a similar manner; but in the salts of those metals of which the protosulphide is dissolved by acids, such as salts of iron, zinc, and manganese, a small quantity of a strong acid entirely prevents precipitation. The sulphides are generally coloured, and many of them are black; hence the effect of hydrosulphuric acid in blackening salts of lead and silver, which renders these compounds so sensitive as tests of the presence of that substance. Hydrosulphuric acid also tarnishes certain metals, such as gold, silver, and brass, so that utensils of which these metals are the basis should not be exposed to this gas.

Bisulphide of hydrogen, HS_2. — When carbonate of potassa is fused with half its weight of sulphur, a persulphide of potassium is formed containing a large excess of sulphur, which affords a solution in water of an orange red colour. The protosulphide of potassium, with hydrochloric acid, gives hydrosulphuric acid and chloride of potassium: HCl and $KS = HS$ and KCl. But when the red solution of persulphide of potassium is poured in a small stream into hydrochloric acid, diluted with two or three volumes of water, while chloride of potassium is formed as before, the hydrosulphuric acid produced combines with another equivalent of sulphur, and forms a yellowish oily fluid, the bisulphide of hydrogen, which falls to the bottom of the acid liquid. Supposing the persulphide of potassium to be a pure bisulphide, then HCl and $KS_2 = HS_2$ and KCl. The result of the combination in this case appears rather capricious; for if the acid and persulphide of potassium be mixed in the other way, — if the acid be added drop by drop to the alkaline sulphide, — then hydrosulphuric acid is evolved, the whole excess of sulphur precipitates, and no persulphide of hydrogen is formed. The oily fluid produced by the first mode of mixing has considerable analogy in its properties to the binoxide of hydrogen, and appears, like that compound, to have a certain degree of stability imparted to it by contact with acids, such as pretty strong hydrochloric acid, while the presence of alkaline bodies, on the contrary, gives its elements a tendency to separate. This decomposition has been taken advantage of to obtain liquid hydrosulphuric acid, by sealing up bisulphide of hydrogen in a Faraday tube (page 77).

Thenard has observed other points of analogy between these compounds. Like binoxide of hydrogen, the bisulphide produces a white spot upon the skin, and destroys vegetable colours, so that it has actually been used in bleaching. The latter compound is also resolved into hydrosulphuric acid and sulphur by all the bodies which effect the transformation of the former into water and oxygen; such as charcoal powder, platinum, iridium, gold, binoxide of manganese, and the oxides of gold and silver, which last, when the bisulphide is dropt upon them, are decomposed in an instant, and even with ignition. The bisulphide of hydrogen undergoes spontaneously the same decomposition, even in well-closed bottles, which are apt, on that account, to be broken. It is soluble in ether, but the solution soon deposits crystals of sulphur. Thenard finds this body not to be uniform in its composition, the proportion of sulphur often exceeding considerably 2 eq. to 1 of hydrogen; but the excess of sulphur is possibly only in solution (Ann. de Ch. 2 ser. xlviii. 79).

SULPHUR AND NITROGEN.

Sulphide of nitrogen; eq. 62 *or* 775; NS_3.—This is a yellow pulverulent solid substance of small stability, and which cannot be formed by the direct union of its elements. The liquid bichloride of sulphur absorbs ammoniacal gas, producing first a flocculent brown matter, $NH_3.SCl_2$, and afterwards, if the action of ammonia is continued, a yellow substance, of which the formula is—

$$2NH_3.SCl_2.$$

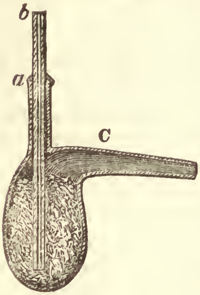
Thrown into water this yellow matter undergoes decomposition, producing hydrochlorate and hyposulphite of ammonia, which dissolve, and a yellow powder, which is a mixture of sulphur and the sulphide of nitrogen. This powder is quickly washed with a little water, dried under the receiver of an air-pump, and finally washed several times with ether, which dissolves out the free sulphur, and leaves the sulphide of nitrogen.

The sulphide of nitrogen is a yellow powder, which, a little above 212°, is decomposed in a gradual manner into sulphur and nitrogen, but when sharply heated, violently and with explosion. It is also slowly decomposed by cold water, but much more rapidly at the temperature of ebullition. The composition of sulphide of nitrogen is determined either by boiling a known quantity in fuming nitric acid, which converts the sulphur into sulphuric acid; or, by heating a mixture of this substance and metallic copper in a glass tube, sealed at one end, and arranged as a retort, so that the gas evolved may be collected. The copper and sulphur unite with avidity, and the nitrogen is disengaged as gas. [*See Supplement*, p. 781.]

SULPHUR AND CARBON.

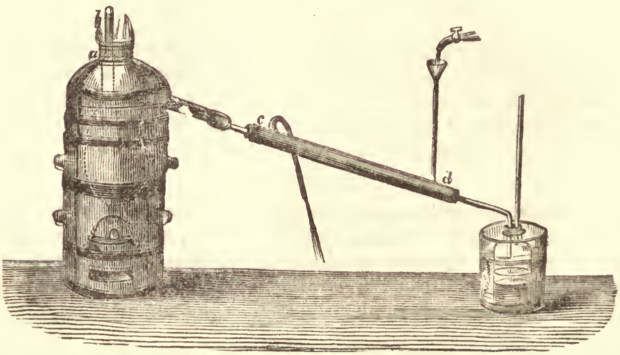
Bisulphide of carbon; sulphocarbonic acid; eq. 38 *or* 475; CS_2.—Charcoal strongly ignited in an atmosphere of sulphur vapour, combines with that element, and forms a compound which holds the same place in the sulphur series that carbonic acid occupies in the oxygen series of compounds. The bisulphide of carbon is a volatile liquid, and may be prepared by distilling, in a porcelain retort, yellow pyrites or bisulphide of iron, with a fourth of its weight of well-dried charcoal, both in the state of fine powder and intimately mixed. The vapour from the retort is conducted to the bottom of a bottle filled with cold water, to condense it. Or sulphur vapour may be sent over fragments of well-dried charcoal in a porcelain or cast iron (not malleable iron) tube, placed across a furnace. The product is generally of a yellow colour, and contains sulphur in solution, to free it from which it is redistilled in a glass retort, by a gentle heat.

FIG. 143.



For preparing a larger quantity of bisulphide of carbon, M. Brunner recommends an earthenware retort of the form C (fig. 143), two-thirds filled with dry charcoal, having a tube, *b*, descending through the tubulure *a*, by which fragments of sulphur can be introduced. The retort is raised to a red heat in a furnace (fig. 144), and the vapour which comes over, carried through a condensing tube, *c d*, kept cold by a stream of water, and ultimately conveyed to the lower part of a bottle surrounded by cold water, and also containing a little water, which floats upon the surface of the condensed liquid and prevents its evaporation. The sulphur is gradually introduced into the retort, and, being immediately converted into vapour, produces the bisulphide of carbon in traversing the incandescent charcoal.

FIG. 144.



The bisulphide of carbon is a colourless liquid, of high refracting power, and sp. gr. 1.272. Its vapour has a tension of 7.38 Paris inches (Marx) at 50°, and the liquid boils at 110°; a cold of —80° can be produced by its evaporation in vacuo. This compound is extremely combustible, taking fire at a temperature which scarcely exceeds the boiling point of mercury. When a few drops of the liquid are thrown into a bottle of oxygen gas, or nitric oxide, a combustible mixture is formed, which burns, when a light is applied to it, with a brilliant flash of flame, but without a violent explosion. The bisulphide of carbon is insoluble in water, but it is soluble in alcohol. It dissolves sulphur, phosphorus, and iodine. The solution of phosphorus in this liquid is used in electrotyping; objects dipped in the solution and dried are left covered by a film of phosphorus, which enables them to obtain a conducting metallic coating when plunged into a solution of copper.

The observed density of the vapour of bisulphide of carbon is 2644.7 (Gay-Lussac). It consists of 2 volumes carbon vapour (density 416) and 2 volumes sulphur vapour (density 2216), condensed into 2 volumes, which form its combining measure; and is therefore quite analogous in condensation to carbonic acid gas. A complete analysis of the bisulphide of carbon is obtained, by passing it in vapour over a mixture of carbonate of soda and oxide of copper in a combustion tube (page 287) at a red heat: the sulphur is oxidized, and remains in combination with the soda as sulphate of soda, while the carbon is burnt also, and disengaged as carbonic acid gas, accompanied by an equal quantity of carbonic acid liberated from the carbonate of soda by the sulphuric acid formed. The carbon alone of this substance may be advantageously determined as carbonic acid, by a similar combustion with chromate of lead.

The bisulphide of carbon is a sulphur acid, and combines with sulphur bases, such as the sulphide of potassium, forming a class of salts which are called sulphocarbonates. Oxygen bases dissolve it slowly, and are converted into a mixture of carbonate and sulphocarbonate: thus 2 equivalents of potassa with 1 of bisulphide of carbon yield 2 equivalents of sulphide of potassium and 1 of carbonic acid, which combine respectively with bisulphide of carbon and potassa.

Solid sulphide of carbon.—The charcoal left in the tube, after the process for the former compound, is much corroded, and contains a portion of sulphur which cannot be expelled from it by heat. Berzelius considered this sulphur as in chemical combination with the carbon. [*See Supplement*, p. 782.]

SECTION VIII.

SELENIUM.

Eq. 39.28 *or* 491 (*F. Sacc*); Se; *density of vapour unknown.*

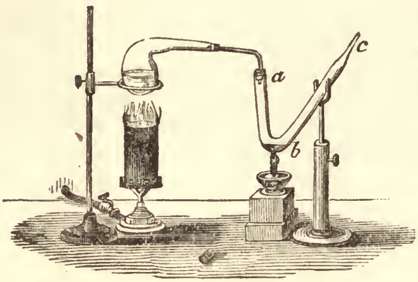
This element was discovered in 1817 by Berzelius, in the sulphur of Fahlun employed in a sulphuric acid manufactory in Sweden, and was named by him selenium, from Σεληνῄ, the moon, on account of its strong analogy to another element, tellurium, which derives its name from *tellus*, the earth. It is one of the least abundant of the elements, but is found in minute quantity in several ores of copper, silver, lead, bismuth, tellurium, and gold, in Sweden and Norway; and in combination with lead, silver, copper, and mercury, in the Hartz. It is extracted from a seleniferous ore of silver of a mine in the latter district, and supplied for sale in little cylinders of the thickness of a goose-quill, and three inches in length, or in the form of small medallions of its discoverer. It has also been found in the Lipari islands associated with sulphur, and can sometimes be detected in the sulphuric acid both of Germany and England. It is separated from its combinations with sulphur and metals by a very complicated process, for which I must refer to the works of Berzelius (Ann. of Phil. vol. xiii. 401; or Ann. de Ch. et de Phys. xi. 160; also Berzelius's Traité, ii. 184, Paris edit. Didot, 1846). [*See Supplement*, p. 784.]

Properties of selenium.—This element is allied to sulphur, and, like that body, exhibits considerable variety in its physical characters. When it cools after being distilled, its surface reflects light like a mirror, has a deep reddish brown colour, with a metallic lustre resembling that of polished blood-stone; its density is between 4.3 and 4.32. When cooled slowly after fusion its surface is rough, of a leaden grey colour, its fracture fine-grained, and the mass resembles exactly a fragment of cobalt. But as selenium does not conduct electricity, and its metallic characters are not constant, it is better classed with the non-metallic bodies. Its powder is of a deep red colour. By heat it is softened, becoming semifluid at 392°, and fusing completely at 482°. It remains a long time soft on cooling, and may then be drawn out like sealing-wax into thin and very flexible threads, which are grey and exhibit a metallic lustre by reflected light, but are transparent and of a ruby red colour by transmitted light. It boils about 1292°, and gives a vapour of a yellow colour, less intense than that of sulphur, but more so than that of chlorine. The density of this vapour has not been ascertained. When heated to the degree of ignition, selenium emits a powerful odour, suggesting that of decaying horse-radish, by means of which the smallest trace of this element may be detected in minerals, when heated before the blow-pipe. The odour was first ascribed to a gaseous oxide of selenium, but it is found by M. Sacc that selenium heated in perfectly dry air is inodorous, and the odour is now referred to the production of a minute quantity of hydroselenic acid.

Selenium combines in two proportions with oxygen, forming selenious acid, which corresponds with sulphurous acid, and selenic acid corresponding with sulphuric acid.

Selenious acid; eq. 55.28 *or* 691; SeO_2.—Selenium does not burn in air, but when strongly heated in the bend of a glass tube *a b c*, (fig. 145), with a current of oxygen passing over it, selenium takes fire and burns with a flame, white at the base, and of a bluish green at the point and edges, but not strongly luminous; selenious acid at the same time condenses in the upper part of the tube as a white sublimate, in long quadrilateral needles. Its vapour has the colour of chlorine. The same acid is the only product of the action of nitric or nitromuriatic acid upon selenium, and is obtained on slowly cooling the liquor in large prismatic crystals, striated lengthwise, which have a considerable resemblance to nitre. These crystals are hydrated selenious acid. This acid is largely soluble, both in water and alcohol. It is decomposed when in solution, and selenium precipitated by zinc, iron, or sulphite of ammonia, with the assistance of a free acid. The selenite of ammonia is also decomposed by heat, and leaves selenium. The selenious is a strong acid, displacing nitric and hydrochloric acids from their combinations, but is displaced in its turn by the more fixed acids, sulphuric, boracic, &c., at a high temperature. (F. Sacc, Annales de Ch. 3 ser. xxi. 119.)

Fig. 145.



Selenic acid, SeO_3.—Selenium is brought to this superior state of oxidation at a high temperature, by fusion with nitre, a process which affords the seleniate of potassa. The selenic acid is precipitated from that salt by the nitrate of lead; and the insoluble seleniate of lead, after being washed, is diffused through water and decomposed by a stream of hydrosulphuric acid, which converts the lead into insoluble sulphide of lead, and liberates selenic acid. A solution of this acid may be concentrated till its boiling point rises to 536°, but above that temperature it changes rapidly into selenious acid, with disengagement of oxygen. Its density is then 2.60, and it contains little more than a single equivalent of water, and therefore corresponds with the protohydrate of sulphuric acid, or oil of vitriol. Selenic acid has not been obtained in the anhydrous condition. Zinc and iron are dissolved by this acid, with the evolution of hydrogen gas; and with the aid of heat it dissolves copper and even gold, an operation in which it is partially converted into selenious acid. But it does not dissolve platinum. To precipitate its selenium, the acid may be digested with hydrochloric acid, which occasions the formation of selenious acid and the evolution of chlorine, and then sulphurous acid throws down the selenium; for it is singular that selenic acid is not de-oxidized by sulphurous acid, although selenious acid is. The compounds of selenic acid with bases, so much resemble the corresponding sulphates, in their crystalline form, colour, and external characters, that they can only be distinguished from them by the property which the seleniates have of detonating when ignited with charcoal, and causing a disengagement of chlorine when heated with hydrochloric acid. To separate the selenic from the sulphuric acid, Berzelius recommends the saturation of the acids with potassa, and the ignition of the dried salt, mixed with sal-ammoniac; the selenic acid is decomposed by the ammonia and reduced to the state of selenium.

SECTION IX.

PHOSPHORUS.

Eq. 400 *or* 32; *P; density of vapour* 4327; □

This remarkable element appears to be essential to the organization of the higher animals, being found in their fluids, and forming, in the state of phosphate of lime, the basis of the solid structure of the bones. It is also found in most plants, and in a few minerals. Phosphorus was first obtained by Brandt of Hamburgh in 1660, but Kunkel first made public a process for preparing it, which was afterwards improved by Margraff and by Scheele. Its ready inflammability, from which phosphorus derived its name, has always made this substance an object of popular interest; while the singularity, importance, and variety of the phosphoric compounds have drawn to them no ordinary share of the attention of chemists.

Preparation.—Phosphorus is not a substance that can be easily prepared on a small scale, but ever since the time of Godfrey Hankwitz, to whom Mr. Boyle communicated a process for preparing it, phosphorus has been manufactured in London, in considerable quantity and of great purity, for the use of chemists. The earth of bones is decomposed by 2-3ds of its weight of sulphuric acid, and the insoluble sulphate of lime separated by filtration from the soluble phosphoric acid, which passes through with a quantity of phosphate of lime in solution. The acid liquor is then evaporated to the consistence of a syrup, and mixed with charcoal to form a soft paste, which is rubbed well in a mortar, and then dried in an iron pot with constant stirring till the mass begins to be red-hot. It is allowed to cool, and introduced as rapidly as possible into a stoneware retort, previously covered with a coating of fire-clay. The beak of the retort is inserted into a wider copper tube of a few feet in length, the free end of which is bent downwards a few inches from its extremity; and the descending portion introduced into a wide-mouthed bottle, containing enough of water to cover the extremity of the tube to the extent of a line or two. The heat of the furnace in which the retort is placed is slowly raised for three or four hours, and then urged vigorously till phosphorus ceases to drop into the water from the copper tube, which may continue from fifteen to thirty hours, according to the size of the retort. Carbon at a high temperature takes oxygen from the phosphoric acid, and becomes carbonic oxide, so that the phosphorus in distilling over is accompanied all along by that gas.

Wöhler recommends, instead of the preceding process, to calcine ivory black, which is a mixture of phosphate of lime and charcoal, with fine quartzy sand and a little more ordinary charcoal, in cylinders of fire-clay, at a very high temperature. Each cylinder has a bent copper tube adapted to it, one branch of which descends into a vessel containing water. The efficiency of Wöhler's process depends upon the silica acting as an acid, and combining with the lime of the phosphate, at a high temperature, while the liberated phosphoric acid is decomposed by the carbon.

Properties.—At the usual temperature phosphorus is a translucent soft solid of a light amber colour, which may be bent or cut with a knife, and the cut surface has a waxy lustre. Its density is 1.77. Phosphorus melts at 108°, undergoing a remarkable dilatation of 0.0134 of its volume, and becoming transparent and colourless immediately before fusion. It forms a transparent liquid, possessing, like most combustible bodies, a high refracting power. At 217° it begins to emit a slight vapour, and boils at 550°, being converted into a vapour which is colourless, of sp. gr. 4355, according to the experiment of Dumas, which coincides almost with the theoretical density 4327. Its combining measure, like that of oxygen, is 1 volume, allowing its equivalent to be 32. When fused and left undisturbed, it sometimes remains liquid for hours at the usual temperature, particularly when covered by an alkaline liquid, but becomes solid when touched. Phosphorus, when very pure, exhibits, by rapid cooling from a high temperature, a modification analogous to that which sulphur undergoes in the same circumstances, but which is not so easily produced. Light causes it, in all circumstances, to assume a red tint; to avoid which action phosphorus is usually preserved in an opaque bottle. Phosphorus cannot be crystallized from a state of fusion, for this substance passes in a gradual manner from the liquid to the solid condition, a circumstance which is always opposed to crystallization; but from its solution in hot naphtha it may be obtained, in cooling, in rhomboidal dodecahedrons of the regular system. It is quite insoluble in water, but soluble to a small extent, with the aid of heat, in fixed and volatile oils, in bisulphide of carbon, of which 100 parts dissolve 20 of phosphorus; in chloride of sulphur, sulphide of phosphorus, and ether.

[The red substance formed by the action of light appears to be a modification of phosphorus exhibiting chemical and physical characters different from its ordinary condition. Red phosphorus is formed not only by exposure to light, but also by keeping phosphorus at a high temperature (464°—482°) for some time, when it assumes a carmine red colour, thickens, and becomes perfectly opaque. This change takes place in an atmosphere of dry carbonic acid, nitrogen or hydrogen. The unaltered portion of the phosphorus is separated from the red variety by means of bisulphide of carbon, in which this latter is insoluble, and it may be purified to a greater extent by boiling it with a solution of potassa, washing with water, then with very dilute nitric acid, and finally again with water.

Red phosphorus is in the form of a scarlet powder. Its density is 1.964. It remains without alteration in the air; and even when heated gradually in a current of air it does not take fire, requiring a temperature of 500° to combine with oxygen and become luminous, and for complete combustion that of 572°. When heated to the boiling point in a gas which has no action on it, common phosphorus results. Chlorine combines with it at common temperatures without the evolution of light. (Schrœter, Journ. Ph. and Ch. Av. 1851).—R. B.] [*See Supplement*, p. 785.]

Phosphorus undergoes oxidation in the open air, and diffuses white vapours, which have a peculiar odour, suggesting to some that of garlic, and are luminous in the dark; and at the same time the phosphorus becomes covered with acid drops, which arise from the phosphorous acid, produced in these circumstances, attracting the humidity of the air. This slow combustion is attended with a sensible evolution of heat, and may terminate in the fusion of the phosphorus, and its inflammation with combustion at a high temperature. There is a necessity for caution, therefore, in handling phosphorus, a burn from this body in a state of ignition being in general exceedingly severe. It is preserved under the surface of water. The low combustion of phosphorus has been particularly studied. It is not observed a few degrees below 32°, but is sensible at that temperature, and increases perceptibly a few degrees above it. The presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus; thus at 66° it is entirely prevented by the presence of,

	Volumes of Air.
1 volume of olefiant gas in	450
1 volume of vapour of sulphuric ether in	150
1 volume of vapour of naphtha in	1820
1 volume of vapour of oil of turpentine in	4444

and the influence of these gases or vapours is not confined to low temperatures, a certain admixture of all of them defending phosphorus from oxidation even at 200°. But on allowing such a gaseous mixture to expand, by diminishing the pressure upon it to a half or a tenth, the phosphorus becomes luminous, and the proportion of foreign gas required to prevent the slow combustion must be greatly increased. The only explanation of this phenomenon which can be offered at present, is that the gases which exert this influence have an attraction for oxygen, and there is reason to believe are themselves undergoing a slow oxidation at the same time. Now when two oxidable bodies are in contact, one of them often takes precedence in combining with oxygen, to the entire exclusion of the other. Potassium is defended from oxidation in air by the same vapours, although to a less degree. (Quarterly Journal of Science, N. S. vol. vi. p. 83). It is curious, that in pure oxygen, phosphorus may remain without oxidating at all, at temperatures below 60°, but an inconsiderable rarefaction of the gas, from diminution of the pressure upon it, will cause the phosphorus to burst into the luminous condition. The dilution of the oxygen with nitrogen, hydrogen, or carbonic acid, produces the same effect. When gradually heated in air, phosphorus generally catches fire, and begins to undergo the high combustion, before its temperature has risen to 140° : of this high combustion, the sole product is phosphoric acid. The inflammability of phosphorus, however, is greatly increased by its impurities, particularly by the presence of the red oxide of phosphorus.

The phosphorus matches now universally employed for procuring a light, are generally the wooden sulphur match, with an additional coating, applied to its extremity, of a paste containing phosphorus, which, when dry, will ignite by friction. The materials added to this paste, to promote the combustion of the phosphorus, are chlorate and nitrate of potassa, or certain metallic oxides, such as the binoxide of manganese or sesquioxide of lead (minium), which abandon readily a portion of their oxygen. The snap, or little detonation which attends the ignition of these matches, is caused by the chlorate of potassa, and is obviated by substituting nitre for that salt; although, to give the proper inflammability, a small proportion of chlorate is found to be indispensable. The phosphorus paste is made by melting phosphorus in a vessel with a certain quantity of water at 120°. The requisite proportion of chlorate or nitrate of potassa is dissolved in this water, and the metallic oxides added, if the latter are used, and then enough of gum to thicken the liquid. The whole are well triturated together, in a mortar, till the globules of phosphorus cease to be visible to the eye; and the mass is coloured blue with Prussian blue, or red with minium. The points of the matches already sulphured are dipped into this paste, so as to cover their extremities, and then cautiously dried in a stove. The gum on drying forms a varnish, which defends the phosphorus from oxidation by the air till the surface is abraded by friction, when the phosphorus first takes fire and communicates its combustion to the sulphur, which again ignites the wood of the match.

Phosphorus is susceptible of four different degrees of oxidation, the highest of which is a powerful acid, while the acid character is not absent even in the lowest. These compounds are: —

Oxide of phosphorus	$2P+O$
Hypophosphorous acid	$P+O$
Phosphorous acid	$P+3O$
Phosphoric acid	$P+5O$

OXIDE OF PHOSPHORUS.

Eq. 72 *or* 900; P_2O.

When burned in air or oxygen, phosphorus generally leaves behind it a small quantity of a red matter, which is an oxide of phosphorus. The same compound is obtained, in larger quantity, by directing a stream of oxygen gas upon melted phosphorus under hot water, and was found by Pelouze to contain 3 equivalents of phosphorus to 2 of oxygen (Annal. de Ch. et de Ph. l. 83).

But this oxide is impure, and the definite oxide appears to have been first obtained by Leverrier (Annal. de Ch. et de. Ph. lxv. 257). His process is to expose to the air small fragments of phosphorus covered by the liquid chloride of phosphorus (PCl_3), in an open bolt-head. Phosphoric acid is formed, and also a yellow matter, which he finds to be a phosphate of the oxide of phosphorus, and which gives a yellow solution with water. This solution is decomposed about 176°, and a flocculent yellow matter subsides, which is a hydrate of the oxide of phosphorus, nearly insoluble in water. This compound abandons its combined water, when dried in vacuo over sulphuric acid, or when cooled below 32°, when the water separates as ice, and oxide of phosphorus remains perfectly pure.

The oxide of phosphorus is a powder of a canary yellow colour, denser than water, and soluble neither in water, alcohol, nor ether. It may be kept in dry air without change. It resists a temperature of 570° without decomposition, but assumes a lively red colour; and does not take fire in the air till heated a little above the boiling point of mercury. This oxide absorbs dry ammoniacal gas, and appears to form feeble combinations with the fixed alkalies. Leverrier assigns to its hydrate the composition P_2O+2HO, and to its phosphate, $2P_2O+3PO_5$.

HYPOPHOSPHOROUS ACID.

Eq. 40 *or* 500; PO; *not isolable. Formula of a Hypophosphite*, $MO.PO+2HO$.

This acid was discovered in 1816 by Dulong (Annal. de Ch. et de Ph. ii. 141). It was obtained by the action of water upon the phosphide of barium, of which the phosphorus of one portion oxidates and becomes the acid in question, at the expense of the water, while the phosphorus of another portion, combining with the hydrogen of the water, produces phosphuretted hydrogen gas. Rose prepares the same hypophosphite of baryta by boiling phosphorus in a solution of caustic baryta, till all the phosphorus disappears and the vapours have no longer the smell of garlic (H. Rose, sur les Hypophosphites, Annal. de Ch. et de Ph. xxxviii. 258). Wurtz uses sulphide of barium. To separate the hypophosphorous acid from the baryta, diluted sulphuric acid is added, which precipitates the latter. To remove again the excess of sulphuric acid unavoidably added, the acid liquid is saturated with oxide of lead, which forms a soluble hypophosphite of lead and an insoluble sulphate of lead. The latter is separated by filtration, and the lead thrown down from the filtrate by a stream of hydrosulphuric acid gas. The acid remaining in solution may be concentrated with caution to the consistence of a thick syrup, but affords no crystals. More strongly heated, the hydrate of hypophosphorous acid undergoes decomposition, being converted into phosphoric acid, with the evolution of phosphuretted hydrogen and a deposition of phosphorus. The anhydrous acid PO has never been obtained, 3 eq. of water being essential to its composition; namely, 1 eq. as base, and 2 eq., which appear to form elements of the acid itself (Wurtz). Hence the formula of the acid is $HO.PO+2HO$; or, believing with Wurtz, that both the oxygen and hydrogen, of 2HO, are negative elements of the acid, like the oxygen in phosphoric acid, the formula is $HO.PH_2O_3$, corresponding with the protohydrate of phosphoric acid $HO.PO_5$.

Hypophosphorous acid is colourless, viscid, and sour to the taste. It withdraws oxygen from the sesquioxide of lead, and some other metallic oxides. When heated with sulphuric acid it changes the latter into sulphurous acid, and also produces a deposit of sulphur, a property by which it is distinguished from phosphorous acid, the complete decomposition of sulphuric acid not being effected by the latter acid. Hypophosphorous acid also decomposes sulphate of copper in solution, producing, when the temperature is only slightly raised, a solid insoluble compound of that metal with hydrogen, the hydride of copper discovered by M. Wurtz, and at the boiling point a deposit of metallic copper with the evolution of hydrogen gas.

The hypophosphites are all soluble in water, and the salts of the magnesian family, such as those of magnesia and cobalt, crystallize well. They are easily obtained by decomposing the hypophosphite of baryta by the soluble sulphates. The dry hypophosphites are permanent in air, but their solutions, evaporated by heat, absorb oxygen. They all contain 2 equivalents of water, which are essential to the constitution of a hypophosphite (Wurtz, Annal. de Ch. et de Ph. 3 sér. vii. 35; and xvi. 190; also, H. Rose, *ib.* viii. 364).

PHOSPHOROUS ACID.

Eq. 56 *or* 800; PO_3. *Formula of a Phosphite,* $2MO.PO_3+HO$.

Preparation. — This acid is the principal product of the slow combustion of phosphorus, but changes after its formation into phosphoric acid, from the further absorption of oxygen from the air. It may be obtained in the anhydrous condition by burning phosphorus with imperfect access of air. Berzelius recommended for this operation a tube of glass, about 10 inches in length and ½ inch in diameter, which is nearly closed at one end, an opening no greater than a large pin-hole being left there, and at a distance of an inch from this extremity the tube is bent at an obtuse angle. A small fragment of phosphorus is introduced into the angle of the tube, and heated till it takes fire. It burns with a pale greenish flame, and the phosphorous acid produced is carried along by the feeble current of air, and condenses in the ascending part of the tube, as a white powder, volatile, but not in the slightest degree crystalline. The phosphorus must not be so much heated as to cause it to sublime unchanged. In contact with air, phosphorous acid is apt to inflame, from the heat occasioned by the condensation of moisture, and is converted into phosphoric acid. The phosphorous acid of the preceding process is immediately soluble in water, while the phosphoric acid, which sometimes accompanies it, remains for a short time undissolved, in the form of white translucent flocks.

Hydrated phosphorous acid is obtained by throwing a few drops of water on the liquid ter-chloride of phosphorus (PCl_3), when that compound evolves hydrochloric acid gas, and gives hydrated phosphorous acid.

$$PCl_3 \text{ and } 3HO = PO_3 \text{ and } 3HCl.$$

The hydrated acid is also obtained by the method of Droquet. Two or three ounces of phosphorus are melted in a cylindrical glass receiver or sealed tube, of 10 or 12 inches in length, and nearly an inch in diameter, and the tube filled up with water. This tube, which will contain a column of fluid phosphorus of 5 or 6 inches in height, is then properly disposed in a bason or bolt-head of warm water, so as to retain the phosphorous fluid. Chlorine gas is conveyed by a quill tube, from a flask in which it is generated, to the bottom of the fluid phosphorus, where combination takes place with ignition, and the chloride of phosphorus is formed. This chloride is dissolved by the water covering the phosphorus, and converted into hydrochloric acid and phosphorous acid. The chlorine must be transmitted very slowly through the phosphorus, as any portion of that gas which reaches the water converts the phosphorous into phosphoric acid; and the absorption of the chlorine by the phosphorus is most complete when it is free from any other gas. When the remaining phosphorus fixes, upon cooling, the acid fluid may be poured off, and concentrated by boiling, till it becomes syrupy and the volatile hydrochloric acid is entirely expelled.

Properties.—In its most concentrated state, the hydrate of phosphorous acid contains three equivalents of water, and crystallizes in transparent prisms. When heated, it is resolved into hydrated phosphoric acid, and pure phosphuretted hydrogen gas, which is not spontaneously inflammable as so prepared. The solution of phosphorous acid absorbs oxygen from the air slowly, if concentrated, but quickly when dilute. Like sulphurous acid, it takes oxygen from the oxide of mercury, when heated with it, and decomposes also the salts of gold and silver. It is one of the more feeble acids.

Phosphites. — The class of phosphites, which has been examined, is bibasic, that is, they contain 2 eq. of base to 1 of phosphorous acid. They also retain 1 eq. of water, the elements of which are proved by Wurtz to enter into the constitution of the acid. Phosphorous acid is thus represented with 5 negative equivalents PHO^4, like phosphoric acid PO_5. Much information respecting the phosphites is contained in the papers of Berzelius. (Annal. de Ch. et de Ph., ii. 151, 217, 329, et x. 278.)

Analysis of phosphorous and hypophosphorous acids. — The composition of both phosphorous and hypophosphorous acid is determined by adding nitric acid to their solutions, by which they are converted into phosphoric acid. But the weight of the resulting phosphoric acid cannot be obtained by simply evaporating its solution to dryness, as that acid retains an indefinite quantity of water in combination. It is necessary to add to the liquid a weighed quantity of oxide of lead, more than sufficient to neutralize the phosphoric acid and what remains of the nitric acid. The whole is then evaporated to dryness in a platinum capsule, and heated sufficiently to expel the nitric acid from the nitrate of lead formed. The water, previously combined with the phosphoric acid, is displaced by the oxide of lead, and escapes, leaving only phosphate of lead with the excess of oxide of lead. This residue is weighed, and the original weight of oxide of lead is deducted from it to obtain the weight of dry phosphoric acid. The composition of phosphoric acid being known (32 phosphorus and 40 oxygen), the quantity of phosphorus in the phosphoric acid of the experiment is obtained by a simple calculation.

Further, if a stream of chlorine gas be transmitted through a solution of hypophosphorous acid, it is converted into phosphoric acid by the oxygen of water which is decomposed. The chlorine uniting with the hydrogen of the water, at the same time, and becoming hydrochloric acid, the quantity of the latter acid produced supplies a measure of the oxygen required to convert the hypophosphorous acid into phosphoric acid.

The composition of phosphorous acid may also be deduced from the analysis of terchloride of phosphorus, which can be made very exactly. One hundred grains of that liquid compound being mixed with water in a flask, it is instantaneously converted into hydrochloric and phosphorous acid; and by the addition of a little nitric acid the latter acid is changed into phosphoric acid. The chloride of silver, precipitated by a solution of nitrate of silver added in excess to the acid liquid, will weigh 310.85 grains, and contains 76.85 grains of chlorine. Hence 100 grains of terchloride of phosphorus contain 76.85 grains of chlorine, and the remaining 23.14 grains is phosphorus. But these numbers are in the proportion 32 phosphorus and 106.5 chlorine, or 1 eq. of the former, and 3 eq. of the latter; giving PCl_3 as the composition of the terchloride of phosphorus. Finally, as phosphorous acid is formed from the terchloride of phosphorus, by replacing the chlorine by an equivalent quantity of oxygen, it follows evidently that the composition of phosphorous acid is PO_3.

PHOSPHORIC ACID.

Eq. 72 *or* 900; PO_5; *forms three hydrates and three classes of salts :*

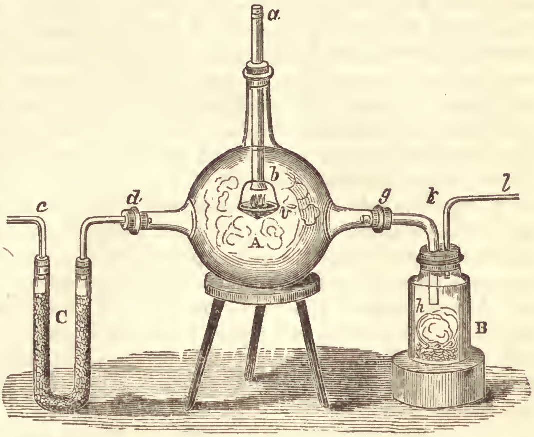
Formula of a Monobasic phosphate, or Metaphosphate	$MO.PO_5$
" " *Bibasic phosphate, or Pyrophosphate*	$2MO.PO_5$
" " *Tribasic phosphate, or Phosphate*	$3MO.PO_5$

Preparation.—To obtain this acid in a state of purity, a convenient process is to set fire to about a drachm of phosphorus upon a little metallic capsule, placed in the centre of a large stone-ware plate, and immediately cover it by a dry bell jar of the largest size. The phosphorus is converted into white flakes of phosphoric acid, which are retained, with very little loss, within the bell jar, and fall upon the plate like snow.

The process may be made a continuous one, and a large quantity of phosphoric acid prepared by the arrangement of figure 146. The phosphorus is burned within a large glass balloon A, having three tubulures, which has been well dried beforehand. The cork of the upper tubulure is traversed by a long tube, *a b*, open at both ends, and about half an inch in diameter, and which descends to about the centre of the globe. A little capsule of platinum or porcelain *v* is attached, by means of platinum wires, below the lower opening of this tube. To the second tubulure *d* a drying tube C, containing pumice soaked in oil of vitriol, is attached;

and to the third tubulure *g* a somewhat wide bent tube, *g h*, of which the other extremity descends into a well-dried bottle B. This last vessel is placed in communication, by means of the tube *k l*, with any aspirating apparatus, by means of which a continuous current of air is determined, which penetrates by the tube C, where it is dried, and traverses the whole apparatus. A fragment of phosphorus is now dropt upon the capsule *v*, by the tube *a b*, lighted by a hot wire, and the upper opening *a* then closed by a cork. When the combustion is completed, another fragment of phosphorus is added, always taking care to dry the fragment carefully with filter paper before its introduction. The phosphoric acid produced is partly deposited in the globe A, and partly carried forward into the bottle B. It is thus obtained quite anhydrous.

Fig. 146.



The dry phosphoric acid is distinguished by the same shade of white, absence of crystallization, and perfect opacity, as solid carbonic acid. Exposed for a few minutes to the air, it deliquesces; and when the solid acid is collected in a wine-glass, and a few drops of water are thrown upon it, it is converted into a hydrate with explosive ebullition, from the heat evolved. The anhydrous acid is perfectly fixed, unless in the presence of aqueous vapour, when it sublimes away, probably in the state of a hydrate.

Phosphorus may likewise be oxidated by means of nitric acid. In this operation, the fuming nitric acid should be diluted with an equal bulk of water, to avoid accidents from the violent action of the acid, which may cause the phosphorus to be projected in a state of ignition; the diluted acid is boiled upon the phosphorus, and being afterwards evaporated to dryness, it yields a hydrated phosphoric acid.

Phosphoric acid is also obtained in large quantity from calcined bones, which are reduced to a fine powder and mixed with 4-5ths of their weight of oil of vitriol, previously diluted with 4 or 5 times its bulk of water, as in the preparation of phosphorus (page 313). Carbonate of ammonia is then added to the filtered solution of phosphoric acid, and the resulting phosphate of ammonia being evaporated to dryness and heated to low redness in a platinum crucible, a hydrated phosphoric acid remains, in a fused state, which is known as glacial phosphoric acid, from its resemblance to ice.

To exhibit many of its properties, phosphoric acid must be first dissolved in water, when the compound is found to be marked by an inconstancy and variableness in its characters, most unusual in a strong acid. This arises from the circumstance that it is not actual phosphoric acid which dissolves in water, any more than it is true sulphuric acid which dissolves in water when oil of vitriol is added to that fluid. It is a hydrate of both acids, which is soluble; the phosphate of water in the one case and the sulphate of water in the other. But the phosphoric acid differs from the sulphuric, in a singular and almost peculiar capacity to form three different salts of water, instead of one only; and these three phosphates of water are all soluble without change, and exhibit properties so different, that they might be supposed to contain three different acids. When the dry acid from the combustion of phosphorus is thrown into water, it produces a mixture, in variable proportions, of the three hydrates; but each of them may be had separately, and in a state of purity, by a particular process. [*See Supplement. p.* 790.]

Terhydrate, or tribasic phosphate of water, $3HO + PO_5$. — The common phosphate of soda of pharmacy may be had recourse to for all the hydrates of phosphoric acid; but it should be first dissolved and crystallized anew to purify it. To a warm solution of the pure phosphate of soda in a bason, a solution of acetate of lead in distilled water is added, so long as it occasions a precipitate; the phosphate of soda requires rather more than an equal weight of acetate of lead. The dense insoluble phosphate of lead which precipitates, is washed, and being afterwards suspended in cold water, is decomposed by a stream of hydrosulphuric acid gas sent through it. The liquid may then be warmed, to expel the excess of hydrosulphuric acid, and filtered from the black sulphide of lead: it is very sour, and contains the terhydrate of phosphoric acid. The characters of this acid solution are, to give a yellow precipitate with nitrate of silver, to give a granular crystalline precipitate with ammonia and sulphate of magnesia — the phosphate of magnesia and ammonia, to yield the common phosphate of soda when neutralized with carbonate of soda, to form salts which have invariably 3 eq. of base to 1 of phosphoric acid, and to be unalterable by boiling its solution or keeping it for any length of time. The class of salts which this hydrate forms are the old phosphates, which have long been known, and it is convenient to allow them to be particularly distinguished as the phosphates or the common phosphates.

Deuto-hydrate of phosphoric acid, or bibasic phosphate of water, $2HO + PO_5$.— Dr. Clark first discovered that when the phosphate of soda is heated to redness, it is completely changed, and after being dissolved in water affords crystals of a new salt, which he named the pyrophosphate of soda,—an observation which led to interesting results. (Ed. Journ. of Science, vol. vii. p. 298, 1826; or Annal. de Ch. et de Phys. xli. 276.) If a solution of this salt, which it is not necessary to crystallize, be precipitated by acetate of lead, the insoluble salt of lead washed and decomposed by hydrosulphuric acid, as before, an acid liquor is obtained which contains the deuto-hydrate of phosphoric acid. It must not be warmed to expel the excess of hydrosulphuric acid, but be left in a shallow bason for twenty-four hours to permit the escape of that gas. This acid, when neutralized with carbonate of soda, gives Dr. Clark's pyrophosphate of soda. It also gives a white precipitate with nitrate of silver; all the salts which it forms have uniformly two eq. of base. They were named the *pyrophosphates*, and since that term has come into use, it is not likely to be superseded by the systematic, but rather inconvenient designation of bibasic phosphates. A dilute solution of the deuto-hydrate of phosphoric acid may be preserved for a month without sensible change, but when the solution is exposed for some time to a high temperature, it passes entirely into the terhydrate.

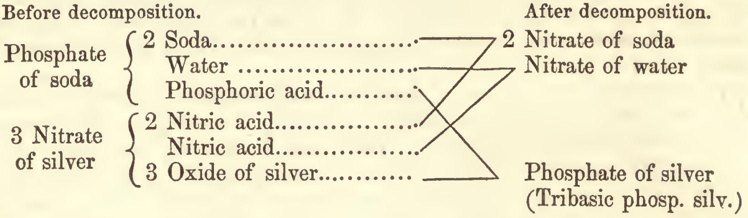
Protohydrate of phosphoric acid.—If the biphosphate of soda be heated to redness, a salt is formed, which treated in a similar manner with the last, gives an acid liquid, containing the protohydrate of phosphoric acid. To prepare the biphosphate itself, a solution of the terhydrate of phosphoric acid is added to a solution of common phosphate of soda, till it is found that a drop of the latter is no longer precipitated by chloride of barium. The biphosphate of soda, which is now in solution, can only be crystallized in cold weather. The glacial phosphoric acid also is in general almost entirely the protohydrate. This hydrate is characterized by producing a white precipitate in solution of albumen, which is not disturbed by the other hydrates, and in solutions of the salts of earths and metallic oxides, precipitates which are remarkable semifluid bodies, or soft solids, without crystallization. All these salts contain only one eq. of base to one of acid, like the protohydrate of the acid itself. The name *metaphosphates* was applied to the class by myself, to mark the cause of the retention of peculiar properties by their acid, when free and in solution; namely, that it was not then simply phosphoric acid, but phosphoric acid *together with* water. (Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid, Phil. Trans. 1833, p. 253; or Phil. Mag. 3d ser., vol. iv. p.

401.) This is the least stable of the hydrates of phosphoric acid, being converted rapidly, by the ebullition of its solution, into the terhydrate. If the terms *metaphosphoric acid* and *pyrophosphoric acid* are employed at all, it is to be remembered that they are applicable to the proto and deutohydrates, and not to the acid itself, which is the same in all the hydrates. But to prevent the chance of misconception, metaphosphate of water and pyrophosphate of water might be substituted for the former terms.

A solution of the terhydrate of phosphoric acid, evaporated in vacuo over sulphuric acid, crystallizes in thin plates, which are extremely deliquescent. The deutohydrate has also been obtained in crystals. When heated to 400°, the terhydrate loses a portion of water, and becomes a mixture of the deuto and protohydrates; and by heating it to redness for some time, the proportion of water may be reduced to one equivalent, or perhaps even less than this; and such is the composition of glacial phosphoric acid. But at that high temperature much of the hydrated phosphoric acid passes off in vapour. The solution of phosphoric acid is not poisonous, nor when concentrated does it act as a cautery, but it injures the teeth from its property of dissolving phosphate of lime. The soluble phosphates, which are not acid, give a precipitate with chloride of barium, which is the phosphate of baryta. This phosphate, in common with all the insoluble phosphates, is dissolved by nitric acid, hydrochloric acid, and even acetic acid, a property by which it is distinguished from sulphate of baryta. A solution of phosphate of lime in phosphoric acid has been prescribed in rickets, a disease which indicates a deficiency of earthy phosphates in the system. The phosphate of soda, also, is given as a mild aperient; its taste is saline, but not disagreeably bitter.

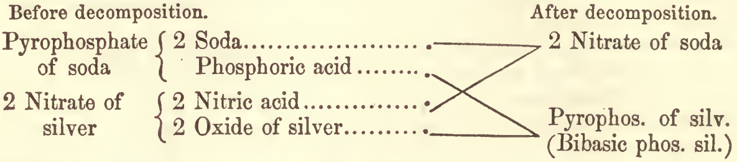
Phosphates.—The formation of three classes of phosphates from the three basic hydrates of phosphoric acid, affords an excellent illustration of the formation of compounds by substitution; the quantity of fixed base, such as soda, with which phosphoric acid combines in the humid way, being entirely regulated by the proportion of water previously in union with the acid, which is simply replaced by the fixed base. Thus, the protohydrate of phosphoric acid combines with no more than one, and the deutohydrate with no more than two equivalents of soda, although a larger quantity of alkali be added to it. The excess of alkali remains free. Again, supposing an equivalent quantity of the terhydrate of phosphoric acid in solution, and one equivalent of soda added to it, one equivalent only of water is displaced, and two retained, and a phosphate formed, containing one of soda and two of water as bases; the salt already adverted to under its old name of biphosphate of soda. Let a second equivalent of soda be added to this salt, and a second basic equivalent of water is displaced, and a tribasic salt produced, containing two of soda and one of water as bases, which is the common phosphate of soda of pharmacy. A third equivalent of soda added to the last salt displaces the last remaining equivalent of basic water, and a tribasic phosphate is formed, of which the whole three equivalents of base are soda, and which has the name of subphosphate of soda. But this last salt can unite with no more soda. The same three salts may be formed by means of the tribasic phosphate of water, in another manner. That acid hydrate decomposes chloride of sodium, but only to a certain extent, expelling hydrochloric acid, so as to acquire one of soda, and becoming $2HO.NaO + PO_5$, or the biphosphate of soda already referred to; the same acid hydrate applied to the carbonate or the acetate of soda, can assume two proportions of soda, displacing twice as much of the weaker carbonic and acetic acids, as of the hydrochloric acid, and so becomes $HO.2NaO + PO_5$, or the common phosphate of soda; and the same acid hydrate applied to the hydrate of soda (caustic soda,) assumes three of soda, and becomes $3NaO + PO_5$, or the subphosphate of soda.

From soluble tribasic phosphates, such as those mentioned, insoluble salts may be precipitated, which are likewise tribasic, by adding solutions of most metallic salts Thus one equivalent of the common phosphate of soda, added to the nitrate of silver in excess, decomposes 3 equivalents of it, and produces the yellow tribasic phosphate of silver, as explained in the following diagram, in which the name of a substance is understood to express one equivalent of it, and the figures, numbers of equivalents:—



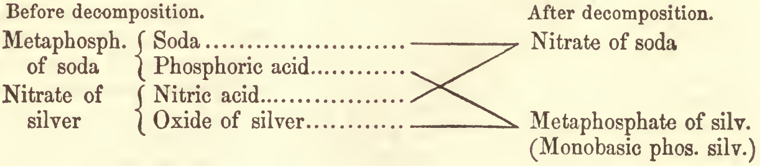
Here, then, is exact mutual decomposition, but it is attended with a phenomenon which does not occur when other neutral salts decompose each other. The liquid does not remain neutral, but becomes highly acid after precipitation; the reason is, that one of the new products is the nitrate of water, or hydrated nitric acid; and consequently the products, although neutral in composition, are not neutral to test paper.

The pyrophosphate of soda, which is bibasic, decomposes, on the other hand, two proportions of nitrate of silver, and gives a pyrophosphate or bibasic phosphate of silver, which is a white precipitate; thus—

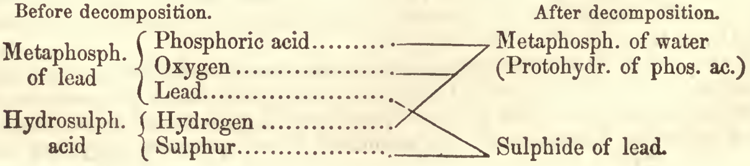


Here there is no salt of water among the products, and consequently the liquid is neutral after precipitation.

The metaphosphate of soda, which is monobasic, like the sulphates, nitrates and other familiar salts, decomposes like these but one proportion of nitrate of silver, and forms a white precipitate; thus—



If acetate or nitrate of lead be substituted for nitrate of silver in these decompositions, a tribasic, bibasic, or monobasic salt of lead is obtained in the same manner; and these salts, again, decomposed by hydrosulphuric acid gas, afford respectively the terhydrate, deutohydrate, and protohydrate of phosphoric acid. The statement of the decomposition of the metaphosphate of lead by hydrosulphuric acid will be sufficient to explain how a hydrate of phosphoric acid comes to be formed in all these cases:—



It will be observed that the hydrosulphuric acid forms 1 equivalent of water, at the same time that it throws down the sulphide of lead. In this phosphate of lead, there is only 1 equivalent of oxide of lead, and consequently only 1 equivalent of water is formed; but if there were 2 or 3 equivalents of oxide, there would be 2 or 3 equivalents of water formed and conveyed to the acid; or the phosphoric acid is always left in combination with as many equivalents of water as it previously possessed of oxide of lead. Thus the different hydrates of phosphoric acid are obtained from the decomposition of the corresponding phosphates of lead.

In no decomposition of this kind is there any transition from one class of phosphates into another, because the decompositions are always mutual, and the products of a neutral character. Hence an argument for retaining the trivial names, common phosphates, pyrophosphates, and metaphosphates, for there is no changing, in decompositions by the humid way, from one to the other, and the salts comport themselves so far quite as if they had different acids. The circumstances may now be noticed in which a transition from the one class to the other does occur:—

1st.—Changes without the intervention of a high temperature. When solutions of the metaphosphate and pyrophosphate of water are warmed, they pass gradually into the state of common phosphate, combining with an additional quantity of water; and the metaphosphate of water appears then to become at once common phosphate, without passing through the intermediate state of hydration of the pyrophosphate. The metaphosphate of baryta also, which is an insoluble salt, is gradually dissolved in boiling water, and becomes common phosphate by assuming 2 eq. of basic water. The easy transition from the one class of phosphates to the other, then witnessed, forbids the supposition that they contain different acids, or different isomeric modifications of phosphoric acid. Indeed, it might as well be supposed that in the protoxide and sesqui-oxide of iron, the metal exists in different isomeric conditions, because these oxides possess peculiar properties, and combine in different proportions with the same acid. Iron in its two oxides gives rise to different compounds, because they are formed by substitution; and phosphoric acid in its three hydrates gives rise to different compounds, from the same cause. The degree of oxidation of the iron and the degree of hydration of the acid are anterior conditions, due to the special unexplained affinities with which each element or compound is invested. It is remarkable that pyrophosphates of potassa and of ammonia exist in solution, and perfectly stable, but not in the dry state. These salts do not crystallize. The pyrophosphate of ammonia, indeed, when allowed to evaporate spontaneously, appears to crystallize, but in the act of becoming solid, it passes into common phosphate (the biphosphate of ammonia, $2HO.NH_4O+PO_5$).

2d.—Changes with the intervention of a high temperature. If a single equivalent of phosphoric acid, anhydrous, or in any state of hydration, be calcined at a temperature which may fall short of a red heat (1°), with 1 equivalent of soda or its carbonate, the metaphosphate of soda will be formed; (2°) with 2 equivalents of soda or its carbonate, the pyrophosphate of soda will be formed; and (3°) with 3 equivalents of soda or its carbonate, a common phosphate of soda will be formed. Hence, the formation of none of these classes is peculiarly the effect of a high temperature. Again, a tribasic phosphate, containing one or two equivalents of a volatile base, such as water or ammonia, loses the volatile base, when ignited, and the acid remains in combination with the fixed base. Hence, common phosphate of soda ($HO.2NaO+PO_5$) is converted by heat into pyrophosphate ($2NaO+PO_5$), the original observation of Dr. Clark; and the biphosphate of soda ($2HO.NaO+PO_5$) into metaphosphate of soda ($NaO+PO_5$). The acid remains in combination with the fixed base, and the salt produced may be dissolved in water without assuming basic water.

The metaphosphate of soda is susceptible of a remarkable conversion, by the agency of a certain temperature, and exhibits a change of nature, without a change of composition, such as often occurs in organic compounds, but rarely admits of so satisfactory an explanation. This particular salt, in common with all the other phosphates, combines with water, which becomes attached to the salt, in the state of constitutional water, or water of crystallization. The metaphosphate of soda, so hydrated, when dried at 212°, retains 1 equivalent of water, but that water is not basic, for, on dissolving the salt again, it is found still to be a metaphosphate. But let this hydrated metaphosphate be heated to 300°, and without losing anything, it changes completely, and becomes a pyrophosphate, — the water which was constitutional before, being now basic. The formulæ of the salt in its two states exhibit to the eye the nature of the internal change which occurs in it:

1.—Hydrated metaphosphate of soda................$NaO.PO_5 + HO$,
2.—Pyrophosphate of soda and water................$NaO.HO + PO_5$.

Phosphates of the form $3MO + 2PO_5$. — The recent investigations of Fleitmann and Henneberg establish the existence of two new classes of phosphates, intermediate between the monobasic and bibasic classes. The soda-salt of the preceding formula is produced by fusing together, in a platinum crucible, 100 parts of anhydrous pyrophosphate of soda and 76.87 parts of metaphosphate of soda: the white crystalline mass which results is reduced to powder, and quickly exhausted with water; for, on long digestion, the ordinary phosphates are obtained. The soda-salt is soluble in about twice its weight of cold water, and has a faint alkaline reaction. It gives, by precipitation with nitrate of silver and with phosphate of magnesia, salts corresponding with the soda-salt, and which have not the properties of a mixture of pyrophosphate and metaphosphate.

Phosphates of the form $6MO + 5PO_5$. — The soda-salt was obtained by fusing together 100 parts by weight of pyrophosphate of soda and 307.5 of metaphosphate. The solution is by no means stable, but gives, when freshly prepared, a precipitate in nitrate of silver, which is readily soluble in excess of the soda-salt, and possesses the composition, when fused, of $6AgO + 5PO_5$. (Liebig's Annalen, lxv. 304.)

Modifications of metaphosphoric acid. — The metaphosphates already described are prepared from the monobasic phosphate of soda in the vitreous condition; this phosphate, when cooled immediately from a state of fusion, remaining a transparent, colourless glass. But if this glassy phosphate be cooled very slowly, a beautiful crystalline mass is obtained. On dissolving it in a small quantity of hot water, the liquid divides into two strata, the more considerable one containing the crystalline salt, and the other a portion of unaltered metaphosphate of soda. The *vitreous metaphosphate*, and all the salts derived from it, are remarkable for not crystallizing, but form liquid or semi-liquid viscid hydrates. But the *crystalline metaphosphate* of soda is described as giving beautiful crystals of the triclinometric system, containing water of crystallization. Its solution is neutral, and has a cooling, pure, saline taste, while the vitreous metaphosphate of soda is insipid. It is rapidly converted into the acid common phosphate by boiling. The corresponding silver-salt is obtained by adding nitrate of silver to a tolerably concentrated solution of the soda-salt. It is white, crystalline, and is represented by the formula $3(AgO.PO_5) + 2HO$.

Phosphates were obtained by Mr. Maddrell, by adding the solution of sulphates of magnesia, nickel, copper, soda, lime, baryta, alumina, to an excess of phosphoric acid, evaporating, to expel the sulphuric acid, and heating to upwards of 600°; in the form of a crystalline granular substance, which were all monobasic. They are all anhydrous, insoluble in water and diluted acids, but generally decomposed by concentrated sulphuric acid, and appear to form a class of metaphosphates different from the preceding two. The magnesian metaphosphates of this class have a disposition to combine with the corresponding soda-salt, when any of that base is present in the phosphoric acid with which they are ignited. The double salt of magnesia and soda is represented by $3(MgO.PO_5) + NaO.PO_5$; that of nickel and soda, by $6(NiO.PO_5) + NaO.PO_5$). (Mem. Chem. Soc. iii. 273.)

The only explanation which can be offered of these modifications of the metaphosphoric acid, is, that they are of a polymeric character; such as $MO.PO_5$; $2MO.2PO_5$; $3MO.3PO_5$, or perhaps even higher multiples of $MO.PO_5$. No data, however, appear to exist by which a place in this polymeric series can be ascribed to the respective modifications with any degree of certainty. MM. Fleitmann and Henneberg, who have lately investigated the subject with much ability, are disposed to represent metaphosphoric acid by $6MO.6PO_5$; and certainly with this proportion of base constant and the phosphoric acid variable, the other classes may be consistently represented:—

Common phosphate	$6MO+2PO_5$
Pyrophosphate	$6MO+3PO_5$
Fleitmann and Henneberg's new phosphates	$6MO+4PO_5$ $6MO+5PO_5$
Metaphosphate	$6MO+6PO_5$

The different classes of phosphates are thus represented as all sex-basic salts, with a different polymeric acid in each, P_2O_{10}, P_3O_{15}, &c. But this theory does not embrace the modifications of metaphosphoric acid, nor will it serve to represent several known double phosphates; such, for instance, as the double pyrophosphate of copper and soda, $3(2NaO.PO_5)+2CuO.PO_5$. [*See Supplement*, p. 786.]

Analysis of phosphoric acid and of the phosphates. — Phosphoric acid is produced when the pentachloride of phosphorus is thrown into water:—

$$PCl_5 \text{ and } 5HO = PO_5 \text{ and } 5HCl.$$

It may be inferred with certainty from this decomposition, that phosphoric acid contains 5 equivalents of oxygen, in the same manner as the composition of phosphorous acid is deduced from the decomposition of the terchloride of phosphorus by water (page 318). The affinity of phosphoric acid for water is very intense, the anhydrous phosphoric acid taking water even from oil of vitriol and eliminating anhydrous sulphuric acid, at a high temperature. As hydrated phosphoric acid cannot be made anhydrous by heat, the proportion of dry acid in a solution of the free acid is determined by adding a known weight of oxide of lead, evaporating to dryness, and heating the residue, as in the case of sulphuric acid. The phosphate of lead formed being anhydrous, the increase of weight which the oxide of lead sustains represents exactly the weight of dry phosphoric acid.

In determining the proportion of phosphoric acid in a salt of an alkaline or earthy base, the acid, if not already in the tribasic form, is first brought to that condition by boiling with a little nitric acid. 1. The excess of nitric acid being then neutralized by ammonia, the phosphate is again dissolved in acetic acid. If the solution contains no sulphuric acid nor chlorine, the phosphoric acid may be entirely separated by the addition of nitrate of lead, in the form of an insoluble phosphate of lead, $2PbO.HO.PO_5$, which washes easily, and loses water and becomes pyrophosphate, $2PbO.PO_5$, when calcined (Heintz). This method is based upon the insolubility of phosphate of lead in acetic acid. 2. Phosphoric acid may also be thrown down from the solution of an alkaline phosphate, by adding first carbonate or hydrochlorate of ammonia and then sulphate of magnesia, when, upon stirring the phosphate of magnesia and ammonia,

$$2MgO.NH_4O.PO_5+12HO,$$

falls as a granular precipitate. This phosphate must be precipitated in an alkaline solution, and washed with water containing hydrochlorate of ammonia, as it is very soluble in acids, and even soluble in a sensible degree in pure water. When ignited it loses its volatile constituents, and remains pyrophosphate of magnesia, $2MgO.PO_5$. 3. The phosphoric acid not being in combination with a base which yields a phosphate insoluble in acetic acid, an addition is made to the liquid, which may be acid, of an excess of the acetate of the sesqui-oxide of iron. The phosphate of sesqui-oxide of iron, $Fe_2O_3.PO_5$, immediately separates as a slightly reddish yellow flaky precipitate, which is collected and washed upon a filter. This phosphate is dissolved off the filter by a few drops of hydrochloric acid, then the salt of iron reduced to the state of protoxide by boiling it with sulphite of soda, and afterwards the quantity of iron ascertained by finding how much of a solution of permanganate of potassa of known composition is required to peroxidize the iron. The phosphate of iron being of known composition, the quantity of phosphoric acid is calculated from the iron, 2 eqs. of that metal being present in the phosphate for 1 eq. of phosphoric acid or of phosphorus; that is, 700 parts iron representing 900 parts phosphoric acid (Raewsky and Marguerite). The acetate of sesqui-oxide of iron, which is not permanent, is best prepared extemporaneously from solutions of 100 parts of iron-alum and of 98 parts of acetate of soda in equal quantities of water, of which equal volumes are mixed at the moment the acetate of iron is required.

In describing the various classes of phosphates, with their relations to each other, I have been thus minute, partly because considerable explanatory detail was required, from the extent of the subject, but principally for the sake of the light which the phosphates throw upon the constitution of the class of organic acids, and upon the function of water in many compounds. Indeed, phosphoric acid is one of the links by which mineral and organic compounds are connected. And it may be reasonably supposed that it is that pliancy of constitution which peculiarly adapts the phosphoric, above all other mineral acids, to the wants of the animal economy.

PHOSPHORUS AND HYDROGEN.

Solid hydride of phosphorus, P_2H.—Magnus formed a phosphide of potassium by fusing phosphorus and potassium under naphtha. When this compound is thrown into water, a compound of phosphorus and hydrogen precipitates in the form of a yellow powder. The solid hydride of phosphorus becomes red when exposed to light; it does not shine in the dark, nor take fire below 320° (160° C.) It is insoluble in water and alcohol, and is decomposed by alkalies, with the formation of oxide of phosphorus, free hydrogen, gaseous phosphuretted hydrogen, and a hypophosphite.

Phosphuretted hydrogen gas; eq. 19 *or* 237.5; PH_3.—This gas, which is remarkable for its occasional spontaneous inflammability in air, was discovered by Gengembre in 1783, and has been successively investigated by several chemists. Its true nature was first ascertained by Rose, who proved it to be a compound having the same proportion of hydrogen as ammoniacal gas, with phosphorus in the place of nitrogen. The pure gas is obtained by heating hydrated phosphorous acid, which is resolved into phosphuretted hydrogen and hydrated phosphoric acid: thus—

$$4(3HO+PO_3) \text{ or } 12HO \text{ and } 4PO_3=PH_3 \text{ and } 9HO+3PO_5.$$

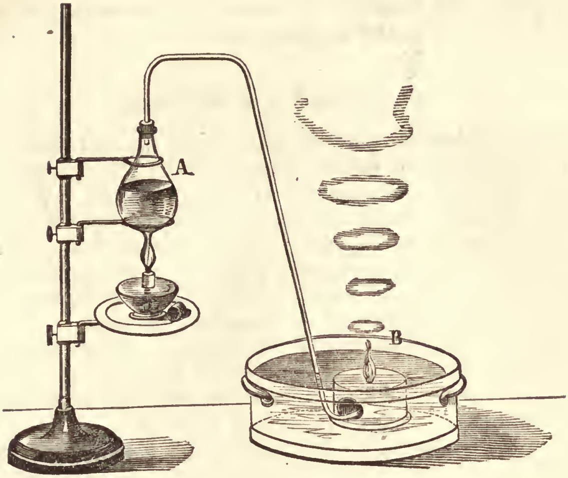
The gas so prepared does not inflame spontaneously when allowed to escape into air, but kindles when a light is applied to it, and burns with the white flame of phosphorus. A little air added to the gas, which had no effect at first, has been observed to produce occasionally an explosion after a time. The gas consists of 1 volume of phosphorus vapour and 6 volumes of hydrogen, condensed into 4 volumes, so that it has the same combining measure as ammoniacal gas. Its density is 1185. Phosphuretted hydrogen has a disagreeable alliaceous odour, is but slightly soluble in water, and has no alkaline reaction.

The same gas, in a self-inflammable state, is obtained by boiling phosphorus with water and an excess of lime, or in a strong solution of caustic potassa, in the flask A (fig. 147), at the water-trough B. The first effect is the formation of hypophosphite of lime, with the evolution of phosphuretted hydrogen gas:

$$4P \text{ and } 3CaO \text{ and } 3HO=PH_3 \text{ and } 3CaO+3PO.$$

Phosphuretted hydrogen is again evolved, but mixed with a considerable quantity of free hydrogen, when the hydrated hypophosphite of lime is evaporated to dryness, phosphate of lime being the residuary product.

Fig. 147.



Each bubble of gas on escaping into air takes fire, and produces a beautiful white wreath of smoke, consisting of phosphoric acid. The spontaneous inflammability is due to the presence of a small quantity of the vapour of a liquid compound of phosphorus and hydrogen, and was first explained by M. P. Thénard.

Phosphuretted hydrogen decomposes some metallic solutions, such as those of copper and mercury, and forms metallic phosphides. When the gas is pure, it is entirely absorbed by sulphate of copper and by chloride of lime. With hydriodic acid, phosphuretted hydrogen forms a crystalline compound, which is interesting from its analogy to sal ammoniac. It may be prepared by mixing together its constituent gases over mercury; or more easily by introducing into a small tubulated retort 60 parts of dry iodine with 15 of phosphorus finely granulated, and mixing these bodies intimately with pounded glass; 8 or 9 parts of water are then added to the mixture, and the vapours which immediately come off are allowed to escape by a glass tube open at both ends, adapted to the beak of the retort in which beautiful small crystals of the salt condense, of a diamond lustre. Rose observed that these crystals do not belong to the Regular System, and are, therefore, not isomorphous with sal ammoniac. They are decomposed by water, with evolution of phosphuretted hydrogen.

Phosphuretted hydrogen combines also, like ammonia, with the perchlorides of tin, titanium, chromium, iron, and antimony, forming white saline bodies. The combination with bichloride of tin is decomposed, with escape of the gas in the non-inflammable state, by water, and in the spontaneously inflammable condition by solution of ammonia.

Liquid hydride of phosphorus, PH_2.—This substance, which was discovered by M. Paul Thénard, is obtained by exposing the phosphuretted hydrogen gas, evolved by the action of water, at 140° (60° C.) on the phosphide of calcium Ca_2P, to a freezing mixture in a condensing tube. It is a colourless liquid, of high refracting power, which does not freeze at —4° (—20° C.), but which a temperature of +86° (30° C.) is sufficient to decompose. It is resolved under the influence of light into the gaseous and solid hydrides of phosphorus. The same decomposition is produced by contact with very different substances, such as alcohol, oil of turpentine, hydrochloric acid, and many pulverulent matters.

This compound is one of the most inflammable substances known, taking fire spontaneously in air, and burning with a dazzling flame. The most minute trace of its vapour, diffusing into the different combustible gases, such as hydrogen, carbonic oxide, cyanogen, olefiant gas, &c., communicates to them, as it does to phosphuretted hydrogen, the property of inflaming spontaneously in air or oxygen. (P. Thénard, Annal. de Ch. et Ph., 3me. sér. xiv. 5.)

PHOSPHORUS AND NITROGEN.

Both chlorides of phosphorus absorb ammoniacal gas, and form solid white compounds. The combination of the terchloride contains $2\frac{1}{2}$ equivalents of ammonia, but that of the perchloride was not found equally definite. When exposed to a strong red heat, without access of oxygen, these compounds leave a white amorphous body, which was supposed to be a nitride of phosphorus, PN_2. (Rose: Annal. de Ch. et Ph., liv. 275.) It is most easily prepared by transmitting a stream of dry carbonic acid gas over the ammoniacal compound, in a tube of hard glass, heated by a charcoal fire, so long as vapours of sal ammoniac sublime.

This substance, which is remarkable for its fixity, is not soluble in any menstruum, nor acted upon by dilute acid or alkaline solutions. It is not affected even when heated in an atmosphere of chlorine or sulphur, but is decomposed when heated in hydrogen gas, with the formation of ammonia.

According to M. Gerhardt, the pentachloride of phosphorus absorbs ammonia, with the evolution of some hydrochloric acid, and the formation of a compound $PCl_3.(NH_2)^2$. The nitride of phosphorus also contains hydrogen, and ought to be represented by the formula PN_2H: its formation from the perchloride of phosphorus and ammonia taking place according to the equation:—

$$PCl_5 \text{ and } 2NH_3 = 5HCl \text{ and } PN_2H.$$

This compound, PN_2H, which is named *Phospham* by Gerhardt, is decomposed by fusion with hydrate of potassa, and converted into ammonia, and the ordinary phosphate of potassa. At a high temperature water acts upon phospham, giving rise to ammonia and phosphoric acid.

PHOSPHORUS AND SULPHUR.—SULPHIDES OF PHOSPHORUS.

Phosphorus and sulphur combine in all proportions, with the evolution of much heat, and sometimes with explosion. These elements most safely unite under hot water, of which the temperature, however, must not exceed 160°; for otherwise hydrosulphuric and phosphoric acids may be produced with such rapidity as to occasion an explosion. The compounds obtained in this manner are of a pale yellow colour,—more fusible and more inflammable than phosphorus itself. They were supposed to be indefinite in composition; but Berzelius has shown that they form a series of sulphides of phosphorus corresponding in composition with the oxides, with one sulphide additional. They are represented by the formulæ—

Subsulphide, P_2S	corresponding	with	Oxide of Phosphorus, P_2O.
Protosulphide, PS	"	"	Hypophosphorous Acid, PO.
Tersulphide, PS_3	"	"	Phosphorous Acid, PO_3.
Pentasulphide, PS_5	"	"	Phosphoric Acid, PO_5.
Persulphide, PS_{12}	without an oxygen analogue.		

These compounds may all be formed directly by fusing sulphur and phosphorus together in the requisite proportions, and are generally crystallizable. The tersulphide was originally obtained by Serullas by the action of hydrosulphuric acid upon the terchloride of phosphorus. They are insoluble in water, alcohol, or ether; but combine readily with alkaline sulphides, and form series of sulphur-salts corresponding with the hypophosphites, phosphites, and phosphates. [*See Supplement*, p. 787.]

[*See Supplement*, p. 787.]

SECTION X.

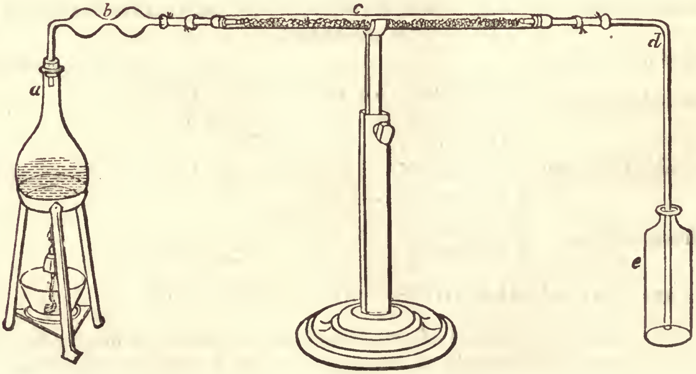
CHLORINE.

Eq. 35.5 *or* 443.75; Cl; *density* 2440; □□.

This substance was discovered by Scheele in 1774, but was believed to be of a compound nature, till Gay-Lussac and Thénard, in 1809, showed that it might reasonably be considered a simple substance. It is to the powerful advocacy of Davy, however, who entered upon the investigation shortly afterwards, that the establishment of the elementary character of chlorine is principally due, and to him it is indebted for the name it now bears, which is derived from χλωρος, yellowish-green, and refers to its colour as a gas, elementary bodies being generally named from some remarkable quality or important circumstance in their history. Chlorine is the leading member of a well-marked natural family, to which also bromine, iodine, and fluorine belong. Phosphorus, carbon, hydrogen, sulphur, and most of the preceding elementary bodies, have little or no action upon each other, or upon the mass of hydrogenous, carbonaceous, and metallic bodies to which they are exposed in the material world; all these substances being too similar in nature to have much affinity for each other. But the class to which chlorine belongs ranks apart, and, with a mutual indifference to each other, they exhibit an intense affinity for the members of the other great and prevailing class — an affinity so general as to give the chlorine family the character of extraordinary chemical activity, and to preclude the possibility of any member of the class existing in a free and uncombined state in nature. The compounds, again, of the chlorine class, with the exception of those of fluorine, are remarkable for solubility, and consequently find a place among the saline constituents of sea water, and are of comparatively rare occurrence in the mineral kingdom; with the single exception of chloride of sodium, which, besides being present in large quantity in sea water, forms extensive beds of rock salt in certain geological formations.

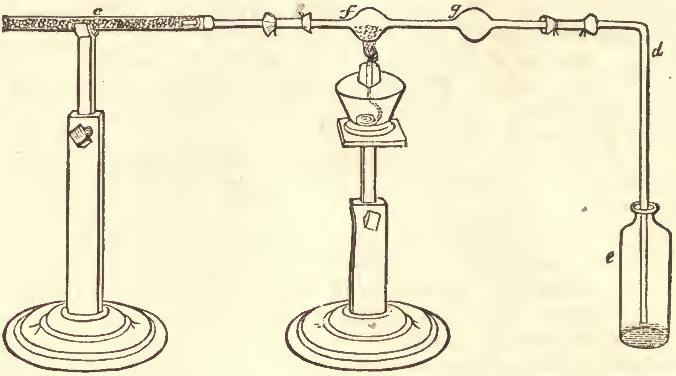
Preparation.—The fuming hydrochloric acid or muriatic acid (as it is also called) of commerce, is a solution in water of hydrochloric gas, a compound of chlorine and hydrogen, from which chlorine gas is easily procured. The liberation of chlorine results from contact of the acid named with binoxide of manganese, and the reaction which then occurs is made most obvious in the following mode of conducting the experiment:—A few ounces of the strongly fuming hydrochloric acid are introduced into a flask *a* (fig. 148), with a perforated cork and tube *b*, upon which a bulb or two have been expanded; and that tube is connected, by means of a short

FIG. 148.



caoutchouc tube, with the drying tube *c*, containing fragments of chloride of calcium, and the last is connected in a similar manner with the exit tube *d*, which descends to the bottom of a dry and empty bottle *e*. Upon applying the spirit-lamp to *a*, the liquid in the flask soon begins to boil, and the hydrochloric gas passes off, depositing, perhaps, a little moisture in the bulbs of *b*, which may be kept cool by wet blotting-paper, and being completely dried in passing through *c*. It is conveyed by *d* to the bottom of the bottle *e*, and finally escapes and produces white fumes in the atmosphere, after displacing the air of that bottle. The hydrochloric gas is obtained in *e* unchanged, and will redden and not bleach a little blue infusion of litmus poured into *e*. But between the tube *c* and *d*, let another tube be now interposed having a pair of bulbs blown upon it *f* and *g* (fig. 149), one of which *f* contains a quantity of pounded anhydrous binoxide of manganese; the bottle *e* remaining as before. Then, upon applying heat to the manganese bulb *f*, the hydrochloric gas will be found to suffer decomposition as it traverses that bulb, its hydrogen uniting with the oxygen of the manganese, and forming water, which will condense in drops in *g*, and disengaged chlorine proceeds on to *e*, in which that gas will be perceptible from its yellow tint, and more so by bleaching the infusion of reddened litmus remaining in *e*. If the transmission of hydrochloric acid over the binoxide of manganese be continued for sufficient time, the latter loses all its oxygen, and the metal remains in the state of protochloride. Indeed, only one-half of the chlorine of the decomposed hydrochloric gas is obtained as gas, the other half being retained by the manganese, as will appear by the following diagram :—

Fig. 149.



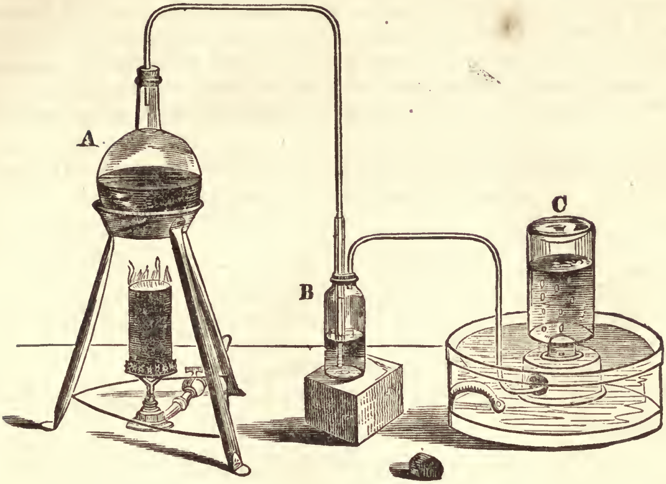
PROCESS FOR CHLORINE FROM HYDROCHLORIC ACID AND BINOXIDE OF MANGANESE.

Before decomposition.		After decomposition.
Hydrochloric acid	Chlorine............	Chlorine.
	Hydrogen..........	Water.
Binoxide of mangan.	Oxygen.............	
	Manganese.........	Chloride of manganese.
	Oxygen.............	
Hydrochloric acid	Chlorine............	
	Hydrogen..........	Water.

Or in symbols :— $MnO_2 + 2HCl = MnCl$ and $2HO$ and Cl.

The most convenient method of preparing chlorine gas is by mixing in a flask A (fig. 150), 1 part of binoxide of manganese with 4 parts of hydrochloric acid,

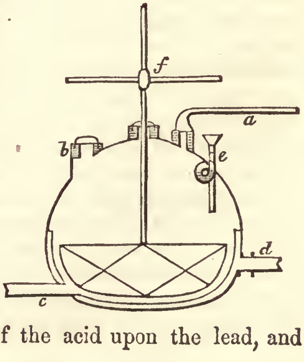
Fig. 150.



diluted with 1 of water. Effervescence, from escape of gas, takes place in the cold, but is greatly promoted by the application of a gentle heat. The gas is collected in C over water, of which the temperature should not be less than 80° or 90°; otherwise a great waste of the gas occurs from its solution in the water, and also a consequent annoyance to the operator from the escape of the chlorine into the atmosphere, by evaporation from the surface of the water-trough. If the gas is not to be used immediately, but preserved, it should be collected in bottles, into which, when filled with gas, their stoppers greased should be inserted before they are removed from the trough. Before the gas obtained by this process can be considered as pure, it should be transmitted through water in a wash-bottle B, to remove hydrochloric acid. If the gas is to be dried, it must be sent through a tube containing chloride of calcium, of two or three feet in length, some difficulty being experienced in drying this gas in a perfect manner, owing to its low diffusive power. Chlorine cannot be collected over mercury, as it combines at once with that metal.

A somewhat different process for the preparation of chlorine is generally followed on the large scale. About 6 parts of manganese with 8 of common salt are introduced into a large leaden vessel, of a form nearly globular, as represented (fig. 151), and 5 or 6 feet in diameter, and to these is added as much of the unconcentrated sulphuric acid of the leaden chambers as is equivalent to 13 parts of oil of vitriol. The leaden vessel is placed in an iron pan, or has an outer casing, *d e*; and to heat the materials, steam is admitted by *d* into the space between the bottom and outer casing. In the figure, which is a section of the leaden retort, *a* represents the tube by which the chlorine escapes, *b* a large opening for introducing the solid material covered by a lid or water valve, its edges dipping into a channel containing water, *e* a twisted leaden funnel for introducing the acid, *f* a wooden agitator, and *c* a discharge tube, by which the waste materials are run off after the process is finished. A retort of lead cannot be used with safety with binoxide of manganese and hydrochloric acid for chlorine, owing to the action of the acid upon the lead, and

Fig. 151.



the evolution of hydrogen gas (which produces a spontaneously-explosive mixture with chlorine), or, it is said, of euchlorine. In the reaction which occurs in the leaden retort, it may be supposed either that hydrochloric acid is first liberated from chloride of sodium by sulphuric acid, and afterwards decomposed by binoxide of manganese, as in the preceding experiment; or that sulphates of manganese and soda are simultaneously formed, and chlorine liberated in consequence, as stated in the following diagram, in which the names express (as usual) single equivalents:—

PROCESS FOR CHLORINE FROM CHLORIDE OF SODIUM (COMMON SALT), BINOXIDE OF MANGANESE, AND SULPHURIC ACID.

Before decomposition.		After decomposition.
Chloride of sodium	Chlorine	Chlorine.
	Sodium	
Sulphuric acid	Sulphuric acid	Sulphate of soda.
Binoxide of manganese	Oxygen	
	Protox. manganese	
Sulphuric acid	Sulphuric acid	Sulph. of mangan.

Or in symbols:

$$NaCl \text{ and } 2SO_3 \text{ and } MnO_2 = NaO.SO_3 \text{ and } MnO.SO_3 \text{ and } Cl.$$

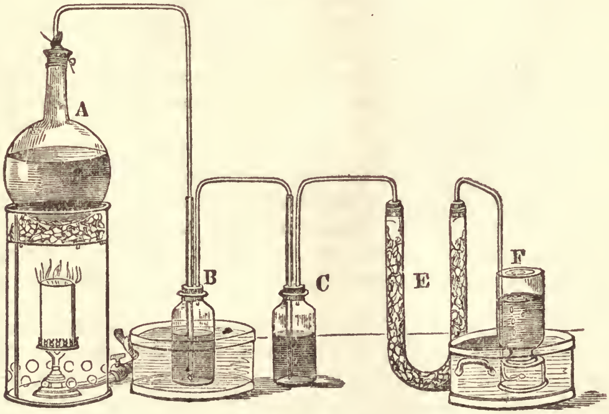
A new manufacturing process for chlorine has lately been applied by Mr. C. Tennant Dunlop, in which the use of binoxido of manganese is superseded by nitric acid. One equivalent of nitric acid is found to communicate two equivalents of oxygen to the hydrochloric acid, and thus evolve two equivalents of chlorine. The decomposed nitric acid is evolved in the form of nitrous acid vapour NO_3, and it is an essential part of the process to absorb that vapour by means of sulphuric acid, and to introduce the nitrous acid in this form into the leaden chamber.

Properties.—Chlorine is a dense gas of a pale yellow colour, having a peculiar suffocating odour, absolutely intolerable even when largely diluted with air, and occasioning great irritation in the trachea, with coughing and oppression of the chest. Some relief from these effects is experienced from the inhalation of the vapour of ether or alcohol. The density of chlorine gas is, by experiment, 2470—by theory, 2440. Under a pressure of about 4 atmospheres, chlorine condenses into a limpid liquid of a bright yellow colour, of sp. gr. about 1.33, and which has not been frozen. Water at 60° dissolves twice its volume of this gas, and acquires the yellowish colour, odour, and other properties of chlorine. To form chlorine-water, a stout bottle filled with the gas at the water-trough, may be closed with a good cork, and removed to a basin of cold water: on loosening the cork with the mouth of the bottle under water, a little water will enter it, from the contraction of the gas by cooling; and this water may be agitated in contact with the gas by a lateral movement of the bottle without removing it from the water; on loosening the cork again, more water will be found to enter the bottle, and by repeating the agitation and admission of water, the whole gas (if pure) is absorbed, and the bottle is in the end filled with water, which of course contains an equal volume of chlorine gas. With water near its freezing point, chlorine combines and forms a crystalline hydrate, which Faraday found to contain 10 eqs. of water. Hence chlorine gas cannot be collected at all over water below 40°. Exposed to light, chlorine water soon loses its properties, water being decomposed and hydrochloric acid formed, with the evolution of oxygen gas. But it may be preserved for a long time in an opaque bottle properly closed. When diluted so far that the water does not contain above 1 or 1½ per cent. of its bulk of chlorine, the odour is by no means strong, and such a solution may be employed in bleaching without inconvenience to the workmen, although a combination of chlorine with hydrate of lime, called the chloride of lime, is generally preferred for that purpose.

Chlorine does not in any circumstances unite directly with oxygen, although several compounds of these elements can be formed; nor is it known to combine directly with nitrogen or carbon. Chlorine and hydrogen gases may be mixed and preserved in the dark without uniting, but combination is determined with explosion by spongy platinum or the electric spark, or by exposure to the direct rays of the sun; even under the diffuse light of day, combination of the gases takes place rapidly, but without explosion. Chlorine, indeed, has a strong affinity for hydrogen, and decomposes most bodies containing that element, hydrochloric acid being always formed. In plunging an ignited taper into chlorine gas, its flame is extinguished, but the column of oily vapour rising from the wick is rekindled by the chlorine, and the hydrogenous part of the combustible continues to burn with a red and smoky flame, which expires on removing the taper into air. Paper dipped in oil of turpentine takes fire spontaneously in this gas, and the oil burns, with the deposition of a large quantity of carbon. The affinity of chlorine for most metals is equally great: antimony, arsenic, and several others, showered in powder into this gas, take fire, and produce a brilliant combustion. Chlorine is absorbed by alcohol and many other organic substances, when it generally eliminates more or less hydrogen, as hydrochloric acid, and enters also by substitution into the original compound, in the place of that hydrogen. It bleaches all vegetable and animal colouring matters, and is believed then generally to act in that manner. The colours are destroyed and cannot be revived by any treatment.

A stream of chlorine gas, thrown into a bottle of dry ammoniacal gas, produces a jet of flame from the combustion of the hydrogen of the ammonia. When chlorine is passed through the undiluted solution of ammonia, the same decomposition takes place, and the reaction is a convenient source of nitrogen gas (page 244).

FIG. 152.



The arrangement represented in fig. 152 may be used for this purpose. It consists of a large globular flask A, in which chlorine is evolved from the usual materials; two wash-bottles, B and C, containing solution of ammonia, the first placed in a bason of cold water to repress its temperature. The nitrogen evolved passes through a U-tube, E, containing fragments of pumice impregnated with a solution of caustic potassa, to absorb any chlorine that may escape the action of the ammonia; and the gas is finally collected in bottles, F, filled with water acidulated with hydrochloric acid, to absorb the vapour of ammonia with which the nitrogen is accompanied.

Chlorine when free is easily recognized by its odour and bleaching power, and by producing both when free and in the soluble chlorides, with nitrate of silver, a white curdy precipitate of chloride of silver, which is soluble in ammonia, but not soluble in cold or boiling nitric acid.

Uses.—Chemistry has presented to the arts few substances of which the applications are more valuable. Chlorine is the discolouring agent of the modern process of bleaching, which, as it is generally conducted with cotton goods, consists of the following operations. The cloth, after being well washed, is boiled first in lime-water and then in caustic soda, which remove from it certain resinous matters soluble in alkali. It is then steeped in a solution of chloride of lime, so dilute as just to taste distinctly, which has little or no perceptible effect in whitening it; but the cloth is afterwards thrown into water acidulated with sulphuric acid, of sp. gr. between 1.010 and 1.020, when a minute disengagement of chlorine takes place throughout the substance of the cloth, and it immediately assumes a bleached appearance. The cloth is boiled a second time with caustic soda, and digested again in dilute chloride of lime and in dilute sulphuric acid, as before. The acid favours the bleaching action, and is required besides to remove the caustic alkali, a portion of which adheres pertinaciously to the cloth. The fibre of the cloth is not injured by dilute sulphuric acid, although digested in it for days, provided the cloth is not allowed to dry with the acid in it, or left above the surface of the liquor. But it is very necessary to wash well after the last *souring*, to get rid of every trace of acid, with which view the cloth may be passed through warm water as a precautionary measure.

Chlorine is had recourse to in disinfecting the wards of hospitals. Mr. Faraday, in fumigating the Millbank Penitentiary, found that a mixture of 1 part of common salt and 1 part of the binoxide of manganese, when acted upon by 2 parts of oil of vitriol previously mixed with 1 part of water (all by weight), and left till cold, produced the best results. Such a mixture, at 60°, in shallow pans of red earthenware, liberated its chlorine gradually but perfectly in four days. The salt and manganese were well mixed, and used in charges of 3½ pounds of the mixture. The acid and water were mixed in a wooden tub, the water being put in first, and then about half the acid: after cooling, the other half was added. The proportions of water and acid are 9 measures of the former to 10 of the latter. (Magazine of Science, 1840, p. 264).

Chlorides.—Chlorine combines with all the metals, and in the same proportions as oxygen. With the exception of the chlorides of silver and lead, and subchlorides of copper and mercury, these compounds are soluble and sapid, and they possess in an eminent degree the saline character. Indeed, common salt, the chloride of sodium, has given its name to the class of salts, and chlorine is the type of salt-radicals or *halogenous* (salt-producing) bodies. Chlorides of metals belonging to different classes often combine together and form double chlorides; the chlorides of the potassium family, in particular, with some chlorides of the magnesian family, as with chloride of copper, with chloride of mercury, with both the chlorides of tin, and with perchlorides generally. A chloride and oxide of the same metal (excepting the potassium family) often combine together, forming *oxichlorides*, which are in general insoluble.

Chlorine is also absorbed by alkaline solutions, and combinations are formed which bleach and exhibit many of the properties of the free element. The chlorine in these compounds, and also in dry chloride of lime, formed by exposing hydrate of lime to chlorine gas, is now generally allowed to exist as hypochlorous acid. They are not permanent compounds, and the chlorine eventually acts upon the metallic oxide, so as to produce a chloride and a chlorate of the metal, as will be afterwards explained.

The following chlorides of the non-metallic elements will now be particularly described:—

Hydrochloric acid	$\mathrm{H\,Cl}$	Chloride of boron	$\mathrm{B\,Cl_3}$
Hypochlorous acid	$\mathrm{Cl\,O}$	Chloride of silicon	$\mathrm{Si\,Cl_3}$
Peroxide of chlorine	$\mathrm{Cl\,O_4}$	Chloride of sulphur	$\mathrm{S_2\,Cl}$
Chloric acid	$\mathrm{Cl\,O_5}$	Bichloride of sulphur	$\mathrm{S\,Cl_2}$
Hyperchloric acid	$\mathrm{Cl\,O_7}$	Terchloride of phosphorus	$\mathrm{P\,Cl_3}$
Chloride of nitrogen	$\mathrm{N\,Cl_3}$	Pentachloride of phosphorus	$\mathrm{P\,Cl_5}$
Chlorocarbonic acid	$\mathrm{CO.Cl}$		

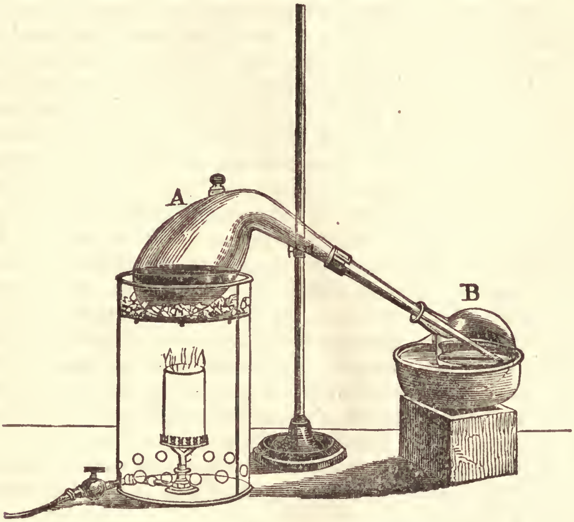
HYDROCHLORIC ACID.

Syn. *Chlorhydric acid, Muriatic acid; Eq.* 36.5 *or* 456.25; ClH; *density* 1269.5; ⊞

This acid is one of the most frequently-employed reagents in chemical operations, and has long been known under the names of spirit of salt, marine acid, and muriatic acid (from murias, sea-salt). It was first obtained by Priestley in its pure form of a gas in 1772.

Preparation.—Hydrochloric acid is always obtained by the action of oil of vitriol upon common salt. When the process is conducted on a small scale and in a glass retort, 3 parts of common salt, 5 oil of vitriol, and 5 water, may be taken. The oil of vitriol being mixed with two parts of the water in a thin flask, and cooled, is poured upon the salt contained in a capacious retort A (fig. 153). A flask B, containing the remaining 3 parts of the water, is then adapted to the retort as a condenser. Upon applying heat to the retort, hydrochloric acid gas comes off, and is condensed in the receiver, affording an aqueous solution of the acid, of about sp. gr. 1.170, which contains 34 per cent. of dry acid; while bisulphate of soda remains in the retort. Supposing 2 equivalents of oil of vitriol and 1 of chloride of sodium to be employed, which the preceding proportions represent, then the rationale of the action is as follows:—

Fig. 153.



PROCESS FOR HYDROCHLORIC ACID.

Before decomposition.				After decomposition.	
58.5	Cloride of sodium	Chlorine.........	35.5	36.5	hydroc. acid
		Sodium..........	23		
49	Oil of vitriol......	Hydrogen.......	1		
		Oxygen.	8		
		Sulphu. acid.....	40	71	sulph. of soda
49	Oil of vitriol..........................		49	49	sulph. of water
156.5			156.5	156.5	

Or in symbols: NaCl and $HO.SO_3 = HCl$ and $NaO.SO_3 + HO.SO_3$.

The hydrochloric acid coming off easily and at a low temperature, when 2 eqs. of sulphuric acid are used, is obtained at once pure and free from sulphuric acid.

This process is more economically conducted on the large scale, as for nitric acid (fig. 116, page 261), in a cast-iron cylinder, about 5 feet in length and 2½ in diameter, laid upon its side, which has moveable ends, generally composed of a thin paving-stone cut into a circular disc and divided into two unequal segments. A charge of three or four hundred pounds of salt is introduced into the retort, and after the bottom is heated, sulphuric acid, as it is withdrawn from the leaden chambers, is added in a gradual manner by means of a long funnel, and in proportion not exceeding 1 equivalent for the chloride of sodium. In such circumstances, the lower part of the cylinder exposed to the sulphuric acid is not much acted upon, while the roof of the cylinder is protected from the hydrochloric acid fumes by a coating of fire-clay or thin bricks. The hydrochloric acid gas is conducted by a glass tube into a series of large jars of salt-glaze ware, connected with each other like Wolfe's bottles, and containing water, in which the acid condenses.

Properties. — Hydrochloric acid is obtained in the state of gas by boiling an ounce or two of the fuming aqueous solution in a small retort, or by pouring oil of vitriol upon a small quantity of salt in a retort, and is collected over mercury. It is an invisible gas, of a pungent acid odour, and produces white fumes, when allowed to escape, by condensing the moisture in the air. By a pressure of 40 atmospheres at 50°, it is condensed into a liquid of sp. gr. 1.27. It is quite irrespirable, but much less irritating than chlorine; it is not decomposed by heat alone, nor when heated in contact with charcoal. Hydrochloric acid extinguishes combustion, and is not made to unite with oxygen by heat; but when electric sparks are passed through a mixture of this gas and oxygen, decomposition takes place to a small extent, water being formed and chlorine liberated. It is composed by volume of one combining measure, or two volumes of each of its constituents, united without condensation; so that its combining measure is 4 volumes, and its theoretical density 1269.5. It may be formed directly by the union of its elements.

If a few drops of water or a fragment of ice be thrown up into a jar of hydrochloric acid over mercury, the gas is completely absorbed in a few seconds; or if a stout bottle filled with this gas be closed by the finger and opened under water, an instantaneous condensation of the gas takes place, water rushing into the bottle as into a vacuum. Dr. Thomson found that 1 cubic inch of water absorbs 418 cubic inches of gas at 69°, and becomes 1.34 cubic inch. He constructed the following table, from experiment, of the specific gravity of hydrochloric acid of determinate strengths (First Principles of Cemistry): —

HYDROCHLORIC ACID.

Atoms of Water to 1 of Acid.	Real Acid in 100 of the liquid.	Specific Gravity.	Atoms of Water to 1 of Acid.	Real Acid in 100 of the liquid.	Specific Gravity.
6	40.66	1.203	14	22.700	1.1060
7	37.00	1.179	15	21.512	1.1008
8	33.95	1.162	16	20.442	1.0960
9	31.35	1.149	17	19.474	1.0902
10	29.13	1.139	18	18.590	1.0860
11	27.21	1.1285	19	17.790	1.0820
12	25.52	1.1197	20	17 051	1.0780
13	24.03	1.1127			

To this may be added the following useful table, for which we are indebted to Mr. E. Davy: —

HYDROCHLORIC ACID.

Specific Gravity.	Quantity of Acid per cent.	Specific Gravity.	Quantity of Acid per cent.
1.21	42.43	1.10	20.20
1.20	40.80	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.05	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.00
1.13	26.26	1.02	4.04
1.12	24.24	1.01	2.02
1.11	22.22		

It thus appears that the strongest hydrochloric acid that can be easily formed contains six eqs. of water: this liquid allows acid to escape when evaporated in air, and comes, according to an observation of my own, to contain 12 eqs. of water to 1 of acid. Distilled in a retort, it was found, by Dr. Dalton, to lose more acid than water till it attained the specific gravity 1.094, when its boiling point attained a maximum of 230°, and the acid then distilled over unchanged. Dr. Clark finds by careful experiments that the acid, which is unalterable by distillation, contains 16.4 equivalents of water.

The concentrated acid is a colourless liquid, fuming strongly in air, highly acid, but less corrosive than sulphuric acid; not poisonous when diluted. It is decomposed by substances which yield oxygen readily, such as metallic peroxides and nitric acid, which cause an evolution of chlorine, by oxidating the hydrogen of the hydrochloric acid. A mixture of 1 measure of nitric and 2 measures of muriatic acid forms *aqua regia,* which dissolves the less oxidable metals, such as gold and platinum.

The hydrochloric acid of commerce has a yellow or straw colour, which is generally due to a little iron, but may be occasionally produced by organic matter, as it is sometimes destroyed by light. This acid is rarely free from sulphuric acid, the presence of which is detected by the appearance of a white precipitate of sulphate of baryta on the addition of chloride of barium to the hydrochloric acid diluted with 4 or 5 times its bulk of distilled water. Sulphurous acid is also occasionally present in commercial hydrochloric acid, and is indicated by the addition of a few crystals of protochloride of tin, which salt decomposes sulphurous acid, and occasions, after standing some time, a brown precipitate containing sulphur in combination with tin (Girardin). To purify hydrochloric acid, it may be diluted till its sp. gr. is about 1.1, for which the strongest acid requires an equal volume of water; and with the addition of a portion of chloride of barium, the acid should then be re-distilled. As the acid brings over enough of water to condense it, Liebig's condensing apparatus (fig. 30, page 73) can be used in this distillation. The pure acid thus obtained is strong enough for most purposes, and has the advantage of not fuming in the air. Hydrochloric acid, like chlorine and the soluble chlorides, gives with nitrate of silver a white curdy precipitate, the chloride of silver, soluble in ammonia, but not dissolved by hot or cold nitric acid.

Hydrochloric acid belongs to the class of hydrogen acids or hydracids. On neutralizing this acid with soda or any other basic oxide, no hydrochlorate of soda is formed; but the hydrogen of the acid with the oxygen of the soda forming water, the chlorine and sodium combine, and produce a metallic chloride. Zinc, and the other metals which dissolve in dilute sulphuric acid, with evolution of hydrogen, dissolve with equal facility in this acid, with the same evolution of hydrogen, and a chloride of the metal is then formed.

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine and oxygen gases in a free state exhibit no disposition to combine with each other in any circumstances, but this is not inconsistent with their forming a series of compounds, as nitrogen and oxygen, which exhibit a similar indifference to each other, also do. The oxides of chlorine are five in number, namely: —

Hypochlorous acid	ClO
Chlorous acid	ClO_3
Peroxide of chlorine, or Hypochloric acid	ClO_4
Chloric acid	ClO_5
Perchloric acid	ClO_7

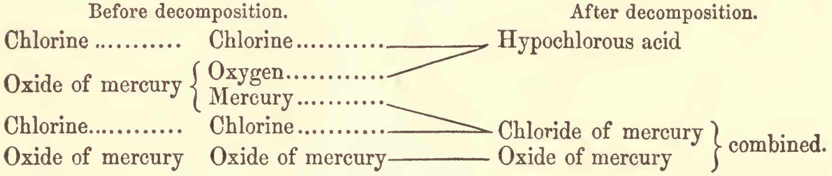
Hypochlorous and chloric acids are always primarily formed by a reaction occurring between chlorine and two different classes of metallic oxides; and the chlorous and perchloric acids, again, are derived from the decomposition of chloric acid.

HYPOCLHLOROUS ACID.

Eq. 43.5; ClO; *density of vapour* 2977; □□

The discovery of this compound in a separate state was made by M. Balard in 1834 (Annal. de Ch. et de Ph. lvii. 225; or Taylor's Scientific Memoirs, i. 269). It was obtained by acting with chlorine upon the red oxide of mercury. If to a two-pound bottle of chlorine gas 300 grains of red oxide of mercury in fine powder be added, with 1½ ounce of water, the chlorine will be found to be rapidly absorbed on agitation. One portion of the chlorine unites with the oxygen of the metallic oxide, and becomes hypochlorous acid, which is dissolved by the water; while another portion forms a chloride with the metal, which chloride unites with a portion of undecomposed oxide, and forms an insoluble oxichloride. The liquid may be poured off and allowed to settle: it is a solution of hypochlorous acid, with generally a little chloride of mercury. This reaction is expressed in the following diagram: —

FORMATION OF HYPOCHLOROUS ACID.



Or in symbols:

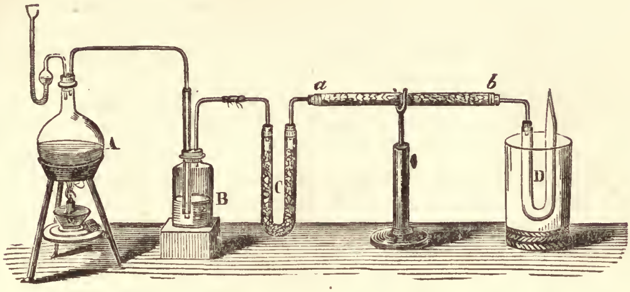
$$2Cl \text{ and } 2HgO = ClO \text{ and } HgCl.HgO.$$

But the oxichloride formed seems not always to contain the same proportion of oxide. The proportion of hypochlorous acid in the liquid may be increased by introducing the same solution into a second bottle of chlorine, with an additional quantity of red oxide of mercury. The oxide of zinc and black oxide of copper, diffused through water, and exposed to chlorine, give rise to a similar formation of hypochlorous acid.

If red oxide of mercury in fine powder be added to chlorine-water so long as the oxide is dissolved, a solution of hypochlorous acid and chloride of mercury is formed, without any insoluble compound: $2Cl$ and $HgO = ClO$ and $HgCl$ (Gay-Lussac).

On the other hand, hypochlorous acid, free from water, and in the liquid state, may be obtained by passing dry chlorine gas in a gradual manner over red oxide of mercury in a glass tube *a b* (fig. 154); care being taken to prevent elevation of temperature, by surrounding the tube with fragments of ice, or immersing it in cold water, as otherwise nothing but oxygen will be disengaged. The chlorine is evolved from the usual materials in the flask A, passed through water in the wash-bottle B to arrest any hydrochloric acid, and afterwards dried over chloride of calcium tube C. Chloride of mercury is formed as in the other processes, and a yellow gas, which is liquefied in the bent tube D, kept cold by a freezing mixture of ice and salt. The oxide of mercury which answers best for this experiment is that precipitated from chloride or nitrate of mercury by potassa, washed and dried at a temperature of about 572° (300° C.) — Regnault's Traité.

Fig. 154.



Hypochlorous acid is a liquid of an orange-yellow colour, which boils at about 68° (20° C.) Its vapour is of a pale yellow colour, very similar to chlorine. It is composed of 2 volumes of chlorine and 1 volume of oxygen, condensed into 2 volumes, which gives a theoretical density of 2992, while 2977 has been obtained by experiment. It is resolved by a slight elevation of temperature into its constituent gases; a property which allows it to be analyzed, by determining the proportions of the mixed chlorine and oxygen gases. Water dissolves about 200 volumes of this gas, and assumes a fine yellow colour.

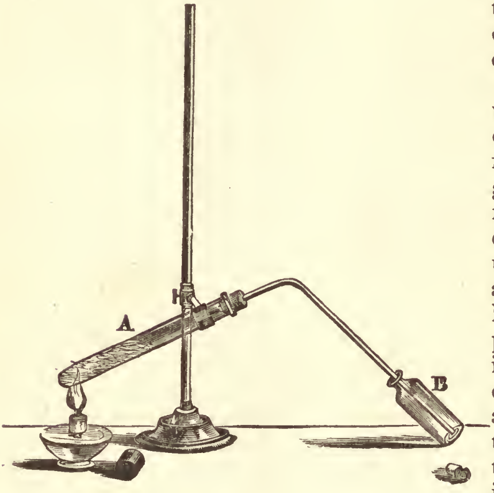
Hypochlorous acid is also formed when chlorine is absorbed by weak solutions of alkalies and by hydrate of lime, and, as the acid of the *bleaching chlorides*, possesses considerable interest. It displaces the carbonic acid of alkaline carbonates, but has not much analogy to other acids. Its taste is extremely strong and acrid, but not sour, and its odour penetrating and different from, although somewhat similar to, chlorine. It attacks the epidermis like nitric acid, and is exceedingly corrosive. It bleaches instantly, like chlorine, and is a powerful oxidizing agent. A concentrated solution of it is exceedingly unstable, small bubbles of chlorine gas being spontaneously evolved and chloric acid formed. This decomposition is promoted by the presence of angular bodies, such as pounded glass, and also by heat and light.

Of the elementary bodies, hydrogen has no action upon hypochlorous acid. Sulphur, selenium, phosphorus, and arsenic, act upon it with great energy, and are all of them raised to their highest degree of oxidation, with the evolution of chlorine gas; selenium even being converted into selenic acid, although it is converted into selenious acid only by the action of nitric acid. Iodine is also converted into iodic acid. Iron filings decompose it immediately, and chlorine gas comes off. Copper and mercury combine with both elements of the acid, and form oxichlorides. Many other metals are not acted upon by it, unless another acid be present, such as zinc, tin, antimony, and lead. Silver has a different action upon hypochlorous acid from that of most bodies, combining with its chlorine, and causing an evolution of oxygen gas. Hydrochloric and hypochlorous acid mutually decompose each other, water being formed, and chlorine liberated; if the liquids are both cooled to a very low degree, before mixture, the chlorine is not disengaged, but combines with water to form the hydrate of chlorine, and causes the liquid to become a solid mass. The presence of soluble chlorides is equally incompatible with the existence of hypochlorous acid.

Hypochlorites. — The direct combination of hypochlorous acid with powerful bases is accompanied by heat, which is apt to convert the hypochlorite into a mixture of chlorate and chloride; but by adding the acid in a gradual manner to the alkaline solution, hypochlorites of potassa, soda, lime, baryta, and strontia, may be formed, and may even be obtained in a solid state by evaporation in vacuo, if a considerable excess of alkali be present, which appears to give a certain degree of stability to these salts. They bleach powerfully, and their odour and colour are identically the same as the corresponding decolourizing compounds of chlorine, formed by exposing solutions of the highly basic oxides named to chlorine gas, from which it is impossible to distinguish them by their physical properties. When chlorine, then, is absorbed by a weak solution of potassa, without heat being applied, the hypochlorite of potassa is formed, with chloride of potassium, both of which remain in solution: —

$$2Cl \text{ and } 2KO = KO.ClO \text{ and } KCl.$$

Fig. 155.



The hypochlorites are salts of a very changeable constitution; a slight increase of temperature, the influence of solar light, even diffused light, converts them into chloride and chlorate.

The *euchlorine* gas of Davy, to which he assigned the composition of hypochlorous acid, has been found to be a mixture of chlorine gas and chlorochloric acid. That mixture is obtained by the action of hydrochloric acid of sp. gr. 1.1 upon chlorate of potassa, aided by a gentle heat. It has a very yellow colour (euchlorine), and explodes feebly when a hot wire is introduced into it, becoming nearly colourless when the chlorochloric acid is decomposed. A tube retort A (fig. 155), is employed for the evolution of this gas, and it is collected in the phial B by displacement.

CHLORIC ACID.

Eq. 75.5 *or* 943.75; $HO.ClO_5$.

When a stream of chlorine gas is transmitted through a strong solution of caustic potassa, the gas is absorbed, and a solution is formed which bleaches at first, but loses that property without any escape of gas, and becomes a mixture of chloride of potassium and chlorate of potassa; the latter of which, being the least soluble, separates in shining tabular crystals. Five equivalents of potassa (the oxide of potassium) are decomposed by 6 of chlorine, 5 of which unite with the potassium, and form 5 equivalents of chloride of potassium, while the 5 of oxygen form chloric acid with the remaining equivalent of chlorine, as stated in the following diagram, in which the numbers express equivalents:—

ACTION OF CHLORINE UPON POTASSA.

Before decomposition.		After decomposition.	
5 Chlorine	5 Chlorine	5 Chloride of Potassium.	
5 Potassa	5 Potassium .... 5 Oxygen		
Chlorine	Chlorine	Chloric acid	Chlorate of potassa.
Potassa	Potassa	Potassa	

Or in symbols: $6Cl$ and $6KO = KO.ClO_5$ and $5KCl$. Such is the nature of the action of chlorine upon the soluble and highly alkaline metallic oxides, when their solutions are concentrated, or heat applied.

The chlorate of baryta may be formed by transmitting chlorine through caustic baryta in the same manner; and from a solution of the pure chlorate of baryta, chloric acid may be obtained by the cautious addition of sulphuric acid, so long as it occasions a precipitate of sulphate of baryta. The solution may be evaporated by a very gentle heat till it becomes a syrupy liquid, which has no odour, but a very acid taste, is decomposed above 100°, and when distilled at a still higher temperature gives water, then a mixture of chlorine and oxygen gases, and hyperchloric acid; which last acid may be prepared in this way without difficulty. Chloric acid is not isolable, being incapable of existing except in combination with water or a fixed base. This acid first reddens litmus paper, but after a time the colour is bleached, and if the acid has been highly concentrated, the paper often takes fire. It dissolves zinc and iron with disengagement of hydrogen. Chloric acid is decomposed by hydrochloric acid, with escape of chlorine, and by most combustible bodies and acids of the lower degrees of oxidation, such as sulphurous and phosphorous acids, which oxidate themselves at its expense.

This acid, when free or in combination, may be recognized by several properties. It is not precipitated by chloride of barium or nitrate of silver, and its salts have no bleaching power; sulphuric acid causes the disengagement from it of a yellow gas, having a peculiar odour, which bleaches strongly; and its salts, when heated to redness, afford oxygen, and deflagrate with combustibles.

Chlorates. — This class of salts is remarkable for a general solubility, like the nitrates. Those of them which are fusible detonate with extreme violence with combustibles. The chlorate of potassa, of which the preparation and properties will be described under the salts of potassa, has become a familiar chemical product, being largely consumed in the manufacture of deflagrating mixtures. The chlorates were at one time termed *hyperoxymuriates*, and their acid, the existence of which was originally observed by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

The composition of chloric acid is ascertained by decomposing a known quantity of chlorate of potassa by heat, and ascertaining the loss of weight which is due to the expulsion of 6 eqs. of oxygen. The chloride of potassium which forms the fixed residue is dissolved, and the chlorine precipitated by nitrate of silver. The chlorine is thus obtained in the form of chloride of silver, of which the composition is known. The relation between the equivalents of chlorine and oxygen is also established by the analysis of the chlorate of potassa (Note, p. 104).

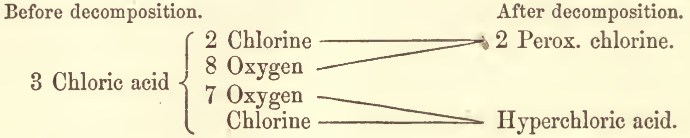
HYPERCHLORIC ACID.

Eq. 91.5 *or* 1143.75; $HO.ClO_7$.

This acid, which is also named perchloric and oxichloric acid, is obtained from chlorate of potassa in different ways. At that particular point of the decomposition of chlorate of potassa by heat, when the evolution of oxygen is about to become very violent, the fused salt is in a pasty state, and contains, as was first observed by

Serullas, a considerable quantity of perchlorate, the oxygen extricated from one portion of chlorate being retained by another portion of the same salt. This salt is rubbed to powder, and dissolved in boiling water, from which the perchlorate is first deposited, on cooling, owing to its sparing solubility. It is stated by M. Millon, that from 50 to 53 per cent. of perchlorate may be obtained by stopping when 9½ litres of gas (580 c. i.) are collected from 100 grammes (1543 grains) of chlorate, instead of 13 litres. (Annal. de Ch et Ph., 3e sér. vii. 335.) The same salt may also be prepared by throwing chlorate of potassa, in fine powder, and well dried, into oil of vitriol gently heated in an open basin, by a few grains at a time, when the liberated chloric acid resolves itself into peroxide of chlorine and hyperchloric acid, the former coming off as a yellow gas; thus:—

RESOLUTION OF CHLORIC ACID INTO PEROXIDE OF CHLORINE AND HYPERCHLORIC ACID.



Of the 3 equivalents of potassa, previously in combination with the chloric acid, one remains with hyperchloric acid as hyperchlorate of potassa, and the other two are converted into bisulphate of potassa. The whole reaction between the acid and salt may, therefore, be thus expressed:—

$$3(KO.ClO_5) \text{ and } 4(HO.SO_3) = 2ClO_4 \text{ and } KO.ClO_7$$
$$\text{and } (2HO.SO_3 + KO.SO_3) \text{ and } 2HO.$$

In conducting this operation, the greatest caution is necessary, owing to the explosive property of peroxide of chlorine; for if the order of mixing the substances be reversed, and the acid poured upon the chlorate, or if too much chlorate be added at a time to the acid, a most violent and dangerous detonation may occur. But this reaction is chiefly interesting as affording peroxide of chlorine; for hyperchlorate of potassa may be obtained from chlorate by the action of nitric acid, lately observed by Professor Penny, without danger or inconvenience. The chlorate is tranquilly decomposed in nitric acid gently heated upon it, the chlorine and oxygen at 3 equivalents of peroxide of chlorine being evolved in a state of mixture and not of combination: the saline residue consists of 3 equivalents of nitrate and 1 of perchlorate of potassa, which may be separated by dissolving them in the smallest adequate quantity of boiling water. On cooling, the perchlorate separates in small shining crystals, which may be dissolved a second time to obtain them perfectly pure.

Perchloric acid may be prepared from the last salt by boiling it with an excess of fluosilicic acid, which forms, with potassa, a salt nearly insoluble. After cooling, a clear liquid is decanted and evaporated by the water-bath. To eliminate a small excess of hydrofluoric acid, a little silica in fine powder is added to the liquid, which at a certain degree of concentration carries off the former as fluosilicic acid. After being still further concentrated, the acid liquid may be distilled in a retort by a sand-bath heat. A very dilute acid comes over first, but the temperature of ebullition rises till it attains 392°, after which the receiver should be changed, because what then passes over is a concentrated acid of sp. gr. 1.65. This acid is a colourless liquid which fumes slightly in the air. It may be still farther concentrated by distilling it with 4 or 5 times its weight of strong sulphuric acid, when the greater part of it is decomposed into chlorine and oxygen; but a portion condenses in a mass of small crystals, and also in long four-sided prismatic needles terminated by dihedral summits, which were found by Serullas to be two different hydrates of the acid, the last containing least water and being most volatile. The crystals and the concentrated solution of the acid have a great affinity for water; the acid itself (ClO_7) appears not to be isolable.

Perchloric acid is much the most stable of the oxides of chlorine; it does not bleach, is not altered by the presence of sulphuric acid, and is not decomposed by sulphurous acid or by hydrosulphuric acid. It dissolves zinc and iron with effervescence, and, in point of affinity, is one of the most powerful acids. Perchloric acid is recognized by producing, with potassa, a salt of the same sparing solubility as bitartrate of potassa. It is an interesting acid from its composition, and as being the most accessible of the small class containing periodic and permanganic acids, to which it belongs. The alkaline perchlorates emit much oxygen when heated, and leave metallic chlorides; they do not deflagrate so powerfully with combustibles as the chlorates.

CHLOROUS ACID.

Eq. 59.5 *or* 743.75; ClO_3; *density* 2.646.

This is a gaseous compound of chlorine and oxygen, which is not liquefied at 5° (—15° C.), and is therefore remarkable for its fixity. It was discovered and studied by M. Millon (Annal. de Ch. et Ph., 3 sér. vii.) Chlorous acid is formed by the deoxidation of chloric acid in various circumstances. It is readily obtained from a mixture of three parts of arsenious acid and four of chlorate of potassa, pulverized together, and made into a thin paste with water; twelve parts of ordinary nitric acid diluted with four of water being added, the whole is introduced into a flask, which is filled to the neck with the mixture, and heated cautiously by a water-bath.

Chlorous acid is a gas of a greenish-yellow colour, of which water dissolves five or six times its volume, assuming a golden-yellow tint of considerable intensity. It bleaches litmus and indigo, but does not attack gold, platinum, nor antimony. It is decomposed by heat, in general at 134.6° (57° C.), into perchloric acid, chlorine, and oxygen: $3ClO_3 = ClO_7$ and 2O and 2Cl. Chlorous acid combines with bases, and forms crystallizable salts; the affinity of this and some other anhydrous acids is gradually exerted, and requires time for its action. On pouring a solution of chlorite of potassa into a solution of nitrate of lead, a yellowish-white precipitate of chlorite of lead is obtained, $PbO.ClO_3$, which is easily subjected to analysis by transforming it into sulphate by means of sulphuric acid; or, if the chlorite of lead be fused in a crucible with carbonate of soda, the whole chlorine of the chlorous acid is obtained in the form of chloride of potassium, and may be precipitated from an acid solution by nitrate of silver, and estimated as chloride of silver.

According to M. Millon, the gas which forms when chlorate of potassa is treated with hydrochloric acid (euchlorine), ought to be considered a compound of chloric and chlorous acid, $2ClO_5.ClO_3$. It is named *chlorochloric acid.* Another double acid, which Millon has named *chloroperchloric acid,* is formed when humid chlorous acid is exposed to light, and condenses as a red liquid, $2ClO_7.ClO_3$.

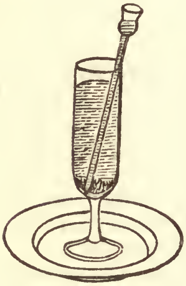
PEROXIDE OF CHLORINE.

Hypochloric acid; eq. 67.5 *or* 843.75: ClO_4.

This substance cannot be obtained in a state of purity without considerable danger. Gay-Lussac recommends, in preparing it, to mix chlorate of potassa in the state of a paste with sulphuric acid previously diluted with half its weight of water and cooled, and to distil the mixture in a small retort by a water-bath. It comes off as a gas, of a yellow colour considerably deeper than chlorine, which cannot be collected over mercury, as it is instantly decomposed by that metal, nor over water, which dissolves it in large quantity. It is composed of 2 volumes of chlorine with 4 volumes of oxygen, condensed into 4 volumes, which gives it a density of 2337.5. This gas is decomposed gradually by light, but between 200° and 212° its elements separate in an instantaneous manner, with the disengagement of light and a violent explosion, which breaks the vessels. Water dissolves about 20 times its volume of this gas: the gas itself is liquefied by cold, and forms a red liquid, which boils at 68° (20° C.) It bleaches damp litmus paper, without first reddening it, and is absorbed by alkaline solutions with the formation of a mixture of a chlorate and chlorite. This compound, then, resembles peroxide of nitrogen, NO_4, and is not a peculiar acid, but may be represented as a compound of chlorous and chloric acids: $2ClO_4 = ClO_3 + ClO_5$.

Peroxide of chlorine has a violent action upon combustibles, kindling phosphorus, sulphur, sugar, and other combustible substances in contact with which it is evolved. Its action upon phosphorus may be shown by throwing a drachm or two of crystallized chlorate of potassa into a deep foot-glass (fig. 156) filled with cold water, to the bottom of which the salt falls without any loss by solution. Oil of vitriol is then conducted to the salt, in a small stream, from a tube funnel, the lower end of which has been drawn out into a jet with a minute opening. A gas of a lively yellow colour is evolved with slight concussions, and immediately dissolved by the water, to which it imparts the same colour. If, while this is occurring, a piece of phosphorus be thrown into the glass, it is ignited by every bubble of gas evolved, and a brilliant combustion is produced under the water, forming a beautiful experiment wholly without danger. If a few grains of chlorate of potassa in fine powder and loaf-sugar be mixed upon paper by the fingers, (rubbing these substances together in a mortar may be attended with a dangerous explosion), and a single drop of sulphuric acid be allowed to fall from a glass rod upon the mixture, an instantaneous deflagration takes place, occasioned by the evolution of the yellow gas, which ignites the mixture. Captain Manby used to fire in this manner the small piece of ordnance, which he proposed, as a life-preserver, to throw a rope over a stranded vessel from the shore; and the same mixture was afterwards employed, with sulphuric acid, in various forms of the instantaneous light-match, all of which, however, are now superseded by other mixtures ignited by friction without sulphuric acid.

FIG. 156.



CHLORINE AND BINOXIDE OF NITROGEN.

Mr. E. Davy appears first to have obtained a gaseous compound of chlorine and binoxide of nitrogen in 1830, and a combination of the same constituents was distilled from *aqua regia* and liquefied by M. Baudrimont in 1843. It is only lately, however, that the nature of the mutual action of nitric and hydrochloric acids has been fully explained by the investigations of M. Gay-Lussac on aqua regia. (Ann. de Ch. et Ph., 3me sér. xxiii. 203; or, Chemical Gazette, 1848, p. 269).

When nitric and hydrochloric acids are mixed, a reaction soon commences if the acids are concentrated; the liquid becomes of a red colour, and effervescence takes place, from the escape of chlorine and a chloro-nitric vapour. On passing this gaseous mixture through a U tube, the angle of which is immersed in a freezing mixture of ice and salt, the chloro-nitric compound condenses as a dark-coloured liquid, and is thus separated from the free chlorine which accompanied it.

Chloro-nitric acid, NO_2Cl_2.—This forms the principal part of the chloro-nitric vapour: it may be represented as a peroxide of nitrogen in which two equivalents of oxygen are replaced by two equivalents of chlorine. A third equivalent of chlorine, due to the third equivalent of oxygen yielded by the nitric acid, is disengaged as gas, and is the agent by which aqua regia dissolves gold, platinum, and other metals having a weak affinity for oxygen, converting them into chlorides: the chloro-nitric acid takes no part in the action. This compound is also formed by the mixture of the two gases in equal volumes, which assume a brilliant orange colour, and suffer a condensation amounting to exactly one-third of their original volume. The theoretical density of this vapour is 1740.2.

Chloro-nitrous acid, NO_2Cl. — This second compound, which corresponds with nitrous acid, NO_3, always appears simultaneously with the other in variable proportions. It is a vaporous liquid of similar properties, of which the vapour density is inferred to be 2259.4. The vapours of both compounds, when conducted into water, are instantly decomposed into hydrochloric acid and peroxide of nitrogen or nitrous acid — a decomposition which affords the means of determining the proportion of chlorine which they contain. The chloro-nitric compounds are also decomposed by mercury, the chlorine combining with the metal and leaving pure binoxide of nitrogen. The solution of the vapours in water decolorizes a solution of permanganate of potassa, owing to the peroxide of nitrogen it contains, but does not bleach indigo because it contains no free chlorine.

CHLORIDE OF NITROGEN.

This is one of the most formidable of explosive compounds, and great caution is necessary in its preparation to avoid accidents. Four ounces of sal ammoniac (which must not smell of animal matter or of nitrate of ammonia), are dissolved in a small quantity of boiling water, filtered, and made up to 3 pounds with distilled water; a two-pound bottle of chlorine is inverted in a basin containing this solution at 80°, being supported by the ring of a retort stand, with its mouth over a small leaden saucer. The chlorine gas is absorbed, and upon the surface of the liquid, which rises into the bottle, an oily substance condenses, which, when it accumulates, precipitates in large drops, and is received in the leaden saucer. During the whole operation, the bottle must not be approached, unless the face is protected by a sheet of wire gauze, and the hands by thick woollen gloves; agitation of the bottle, to make the suspended drop fall, is a common cause of explosion. The leaden saucer, when it contains the chlorine, may be withdrawn from under the bottle, without disturbing the latter, and then no harm can result from the explosion, if it does not occur in contact with glass.

M. Balard finds that this compound may also be produced by suspending a mass of sulphate of ammonia in a strong solution of hypochlorous acid.

The chloride of nitrogen is a volatile oleaginous liquid of a deep yellow colour, and sp. gr. 1.653, of which the vapour is irritating like chlorine, and attacks the eyes. It may be distilled at 160°, but effervesces strongly at 200°, and explodes between 205° and 212°, producing a very loud detonation, and shattering to pieces glass or cast-iron, but producing merely an indentation in a leaden cup. It is resolved into chlorine and nitrogen gases, the instantaneous production of which with heat and light, is the cause of the violence of the explosion. The chloride of nitrogen is decomposed by most organic matters containing hydrogen; and may be safely exploded by touching it with the point of a cane-rod, which has been previously dipped in oil of turpentine.

This compound is represented by NCl_4, but the properties of this compound render its accurate analysis almost impossible, and the correctness of the formula usually assigned to it is very doubtful. M. Millon has shown that it may contain hydrogen, and is possibly a nitride of chlorine with ammonia, $Cl_3N + 2H_3N$. He formed from it corresponding compounds, containing bromine, iodine, and cyanogen, by double decomposition; a bromide, iodide, or cyanide of potassium being introduced into the chloride of nitrogen for that purpose. (Annales de Chim. et de Phys. lxix. 75.) [*See Supplement*, p. 791.

CHLORIDES OF CARBON.

Sesquichloride of carbon, C_4Cl_6. — The compounds of these elements are not formed directly, but were produced by Mr. Faraday by the action of chlorine upon a certain compound of carbon and hydrogen; the circumstances of their formation were explained with singular felicity by M. Regnault. Chlorine and olefiant gas C_4H_4 combine together in equal volumes, and condense as Dutch liquid (page 286).

Chemists are now generally agreed that the rational formula of this liquid is not C_4H_4+2Cl, but that its elements are thus arranged :—

Dutch liquid..........................$C_4H_3.Cl+HCl$.

It is considered a combination of hydrochloric acid HCl, with the chloride of acetyl $C_4H_3.Cl$. When a stream of chlorine gas is transmitted through Dutch liquid, a second eq. of hydrogen is carried off, as hydrochloric acid, and 1 eq. of chlorine left in its place; thus Dutch liquid, $C_4H_3Cl+HCl$ becomes—

$$C_4H_2Cl_2+HCl.$$

This second product, which is a liquid, being submitted to the action of a stream of chlorine, gives rise to a third liquid product, in which the hydrochloric acid of the last formula disappears, and the remaining portion assumes 2 additional eqs. of chlorine, forming —

$$C_4H_2Cl_4.$$

This third liquid is changed by the prolonged action of chlorine into the sesquichloride of carbon, but to hasten the action it is convenient to conduct the operation in the light of the sun; its two remaining eqs. of hydrogen being carried off in the form of hydrochloric acid, and 2 eqs. of chlorine left in their place, which gives the formula

Sesquichloride of carbon...............C_4Cl_6, or $C_4Cl_4+Cl_2$.

This view of the derivation and constitution of the sesquichloride of carbon is confirmed by the density of its vapour, which Regnault found by experiment to be 8157. It should from its formula contain

8 volumes carbon vapour	3371
12 volumes chlorine	29284
	32655

If these form a combining measure of 4 volumes, the most usual of all combining measures, the weight of 1 volume, or density of the vapour, is 8164, which almost coincides with the experimental result.[1]

The sesquichloride of carbon is a volatile crystalline solid, having an aromatic odour resembling that of camphor, fusible at 320° and boiling at 360° (Faraday), of sp. gr. 2, soluble in alcohol, ether, and oils. It was prepared by Mr. Faraday by exposing Dutch liquid to sunlight in an atmosphere of chlorine, which was several times renewed as the chlorine was absorbed.

Protochloride of carbon, C_4Cl_4.—This compound was prepared by Faraday by passing the vapour of the sesquichloride through a glass tube filled with fragments of glass, and heated to redness. A great quantity of chlorine becomes free, and a colourless liquid is obtained, which when purified from sesquichloride of carbon and chlorine as much as possible, boils at 248° (Regnault), has a sp. gr. of 1.5526, and in its chemical relations is very analogous to the sesquichloride of carbon. The density of the vapour of the protochloride decides the nature of its constitution. It was found by Regnault to be 5820, which corresponds to the composition by volume :—

8 volumes carbon vapour	3371
8 volumes chlorine	19523
	22894

$$\text{Density} = \frac{22894}{4} = 5724.$$

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[1] Regnault, De l'Action du Chlore sur la liqueur des Hollandais et sur le Chlorure d'Aldéhydène. Ann. de Ch. et de Ph. t. 69, p. 151. Idem, Sur les Chlorures de Carbon, ib. t. 70, p. 104.

It must, therefore, contain 4 eqs. of carbon and 4 of chlorine, and its formula be C_4Cl_4, or it represents olefiant gas C_4H_4 with its whole hydrogen replaced by chlorine. It is interesting to observe how a body retains, after so many mutations, such distinct traces of its origin. From its analysis it might be a compound of single equivalents, C Cl, of the simplest nature, and so it was considered when named protochloride of carbon.

Subchloride of carbon, C_4Cl_2.—Another compound of this class exists, of which a specimen produced accidentally was examined by Messrs. Phillips and Faraday. Regnault has formed it by making the preceding liquid compound pass several times through a tube at a bright red heat. It condenses in the coldest parts of the tube in very fine silky crystals, which may be taken up by ether, and obtained perfectly pure by a second sublimation.

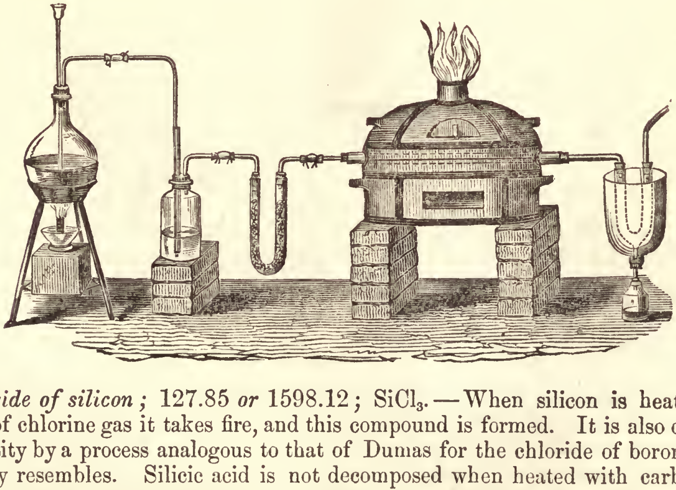
Perchloride of carbon, C_2Cl_4, was obtained by Regnault from the prolonged action of chlorine on hydrochloric ether, wood-spirit, or chloroform, and by M. Kolbe by passing chlorine gas impregnated with the vapour of bisulphide of carbon through a porcelain tube heated to redness. It is a colourless liquid, of density 1.6, boiling at 172° (78° C.) By passing the vapour of this chloride through a tube heated to dull redness, Regnault obtained another chloride of carbon, isomeric with Faraday's sesquichloride, but of which the vapour density was 4.082. Kolbe formed a crystallizable compound of perchloride of carbon and sulphurous acid, which has the formula $2(SO_2)+C_2Cl_4$.

Another chloride of carbon, of the formula $C_{20}Cl_8$, was obtained by M. Laurent, by the action of chlorine upon naphthaline, $C_{20}H_8$, in the form of a crystalline solid, soluble in boiling petroleum.

Chloroxicarbonic gas, CO.Cl.—This gas is formed by exposing equal measures of chlorine and carbonic oxide to sunshine, when rapid but silent combination ensues, and they contract to one half their volume (page 275). [*See Supplement*, p. 791.]

Chloride of boron, B Cl_3.—A gaseous compound of these elements was obtained by Berzelius, by transmitting chlorine over boron heated in a glass tube, and by Dumas by transmitting the same gas over a mixture of boracic acid and carbon ignited in a porcelain tube placed across a furnace (fig. 157). Its density was found to be 4079 by Dumas, and it is considered a terchloride.

FIG. 157.



Chloride of silicon; 127.85 *or* 1598.12; $SiCl_3$.—When silicon is heated in a stream of chlorine gas it takes fire, and this compound is formed. It is also obtained in quantity by a process analogous to that of Dumas for the chloride of boron, which it greatly resembles. Silicic acid is not decomposed when heated with carbon, but if chlorine gas be present, then the simultaneous action of the latter element upon the silicon favours the action of the carbon on the oxygen, and carbonic oxide with chloride of silicon results. Precipitated silica (page 290), which is in a highly divided state, is mixed with an equal weight of lamp-black, and made into a stiff paste with a little oil; this is divided into balls, which are rolled in charcoal powder, and then exposed to a strong red heat in a covered crucible. These ignited balls form the mixture of silica and charcoal which is introduced into the porcelain tube (fig. 157), and heated strongly by a charcoal furnace, while chlorine gas, washed by water and dried in a chloride of calcium tube, is carried through the porcelain tube. The chloride of silicon is condensed in a U tube placed in an inverted bell-jar, with an opening at the lower part; a short straight tube is cemented to the lower part of the U tube, and, passing through the tubulure of the jar, terminates in a small, thoroughly dry bottle, where the liquefied chloride of silicon is collected. (Regnault's Traité).

The chloride of silicon is a colourless, highly mobile liquid, of density 1.52; which boils at 138° (59° C.), and fumes in the air. It is instantly decomposed by contact with water, and resolved into hydrochloric acid and silica:—

$$SiCl_3 \text{ and } 3HO = SiO_3 \text{ and } 3HCl.$$

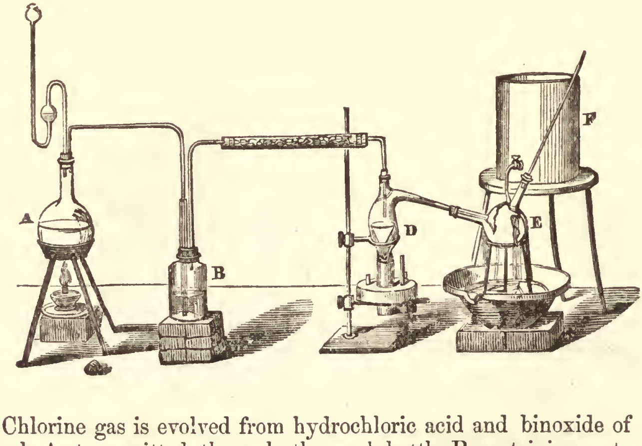
This property affords the means of analyzing the chloride of silicon, as the chlorine of the hydrochloric acid formed may be precipitated by nitrate of silver, and its amount determined. The proportion of oxygen in silicic acid may also be deduced from the same experiment, as the oxygen must necessarily be equivalent to the chlorine in the chloride.

CHLORINE AND SULPHUR.

Chlorine and sulphur appear to combine in several different proportions, some of these compounds being formed only in combination with certain other chlorides. But two compounds of these elements have been obtained in a separate state.*

Subchloride of sulphur; 67.5 *or* 843.75; S_2Cl.—This compound was first obtained by Dr. T. Thomson in 1804. To prepare it, a few ounces of flowers of sulphur are introduced into the tubulated retort D (fig. 158), and fused by a lamp below. Chlorine gas is evolved from hydrochloric acid and binoxide of manganese in the flask A, transmitted through the wash-bottle B containing water, and afterwards dried by chloride of calcium, before the gas reaches the sulphur in D. The chlorine is rapidly absorbed, and a yellowish red dense liquid distils over, and is condensed in the flask with two openings E, which is kept cool by a stream of water from F. It contains an excess of sulphur in solution, but is obtained pure by

FIG. 158.



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* [*See Supplement*, p. 793.]

redistilling the liquid at a moderate temperature (Rose, Annal. de Ch. et de Ph. l. 92). The subchloride of sulphur boils at about 280°, and has a disagreeable odour, somewhat resembling that of sea-weed, but much stronger. Its density in the liquid state is 1.687; the density of its vapour has been found 4668 by experiment. This compound is capable of dissolving a large quantity of sulphur, which may be obtained in crystals from a solution saturated at a high temperature. It is decomposed by water, and hydrochloric acid with acids of sulphur formed.

In one of the processes for *vulcanizing* caoutchouc, the subchloride of sulphur is employed. This compound is dissolved in 50 times its bulk of well rectified coal naphtha, and the articles of caoutchouc immersed in the fluid for one minute, then taken out and dried without heat. The caoutchouc thus acquires a small portion of sulphur, with which it appears to combine, and is improved greatly in elasticity and strength.

Protochloride of sulphur, 51.5 *or* 643.75; SCl. — If chlorine be passed through the former compound, the gas is absorbed in large quantity, and a liquid compound of a deep red colour formed, which contains twice as much chlorine. The new compound dissolves an excess of chlorine, which must be expelled by ebullition. When pure, this chloride boils at 147°.2 (64° C.) Its density in the liquid form is 1.620, and in the state of vapour 3549. It is decomposed like the preceding compound when agitated with water, all its chlorine becoming hydrochloric acid, the quantity of which may be determined by the usual means. Polythionic acids are also formed, with a deposit of sulphur. This compound, of which the formula is SCl, may correspond with hypochlorous acid ClO, or with hyposulphurous acid; but the subchloride of sulphur, S_2Cl, has no analogue among the known compounds of oxygen and chlorine, or of oxygen and sulphur.

When chlorine is passed over the bisulphide of tin, the gas is absorbed, the sulphide fuses, and a compound is formed in yellow crystals, which consists of $SnCl_2 + SCl_2$. The sulphur of the sulphide of titanium and of the sulphides of antimony and arsenic is converted by chlorine in the same manner into bichloride, and the metal itself obtains the same proportions of chlorine as it had of sulphur previously, the new products also remaining in combination with each other (Rose, Annal. de Ch. et de Ph. lxx. 270).

CHLORIDES OF PHOSPHORUS.*

Terchloride of phosphorus, PCl_3. — This chloride, which corresponds with phosphorous acid, is obtained by passing chlorine through melted phosphorus, as for chloride of sulphur (fig. 158); a clear and volatile liquid distils over, of sp. gr. 1.45. It is capable of dissolving phosphorus; when mixed with water, it is resolved into hydrochloric and phosphorous acids.

Pentachloride of phosphorus, PCl_5. — Phosphorus takes fire spontaneously in a vessel of dry chlorine, and produces a snow-white woolly sublimate, which is very volatile, rising in vapour below 212°. It is converted by water into hydrochloric and phosphoric acids.

The variation of the vapour-density of this substance observed by M. Cahours, has already been referred to (page 138). This compound is considered by Cahours as a direct combination of the terchloride with 2 eq. chlorine, $PCl_3 + Cl_2$.

Chloroxide of phosphorus, PCl_3O_2. — The vapour of water produces with the pentachloride of phosphorus a compound so named, discovered by M. Wurtz. It is a colourless and very limpid liquid, of density 1.7, which fumes in air. It is decomposed by water.

Chloro-sulphide of phosphorus, PCl_3S_2. — It was discovered by Serullas, and is obtained by the action of hydrosulphuric acid on the pentachloride of phosphorus. It is liquid, boils at 262° (128° C.); is not decomposed by water. The alkaline oxides transform it into a *sulphoxiphosphate*, a metallic chloride being produced at the same time: PCl_3S_2 and $6NaO = 3NaO.PO_3S_2$ and $3NaCl$.

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* [*See Supplement*, p. 794.]

These salts, which correspond with the tribasic phosphates, may be crystallized. The sulphoxiphosphate of soda crystallizes with 24 eq. water, $3NaO.PO_3S_2+24HO$, and has, therefore, a composition exactly similar to the phosphate of soda, $3NaO.PO_5+24HO$, but the form is different. Here, then, sulphur is not isomorphous with oxygen (Wurtz, Annal. de Ch. 3me sér. xx. 472).

SECTION XI.

BROMINE.

Eq. 78.26 *or* 978.30; Br; *density of vapour* 5393; ◫.

This element was discovered by M. Balard of Montpellier in 1826. Its name is derived from Βρωμος, mal-odour, and was applied to it on account of its strong and disagreeable odour. Like the other members of the chlorine family, it is found principally in solution, being present in an exceedingly minute but appreciable proportion in sea-water, under the form of bromide of sodium or magnesium, also in the water of the Dead Sea, and in nearly all the saline springs of Europe, of which that of Theodorshall near Kreuznach in Germany is the principal source of bromine, as an article of commerce. Bromine is interesting from its chemical relations, particularly from the extraordinary parallelism in properties with chlorine which it exhibits.

Preparation. — Bromine in combination is discovered by means of chlorine-water, a few drops of which cause the colourless solution of a bromide to become orange-yellow, like nitrous acid, by disengaging bromine, while an excess of chlorine weakens the indication, by forming a chloride of bromine which is nearly colourless. Before the application of this test, the saline water in which bromine is contained must always be greatly concentrated, and, indeed, the greater part of its salts should be separated by crystallization. The bromides are highly soluble, and remain in the crystallizable liquor which is called the mother-ley, or bittern in the case of sea-water. The bromide of magnesium may lose hydrobromic acid during the farther concentration of the mother-ley, by evaporation, on which account Desfosses recommends the addition of hydrate of lime to the liquid, which throws down magnesia, and produces a bromide of calcium which may be evaporated without loss of bromine. Instead of using free chlorine to extricate the bromine, binoxide of manganese and a little hydrochloric acid may be added to the liquid. Upon distilling, bromine is liberated and comes off completely before the liquid boils. The watery vapour which condenses in the receiver along with the bromine contains a portion of chloride of bromine, from which the bromine may be separated by adding baryta to the liquid, and forming a chloride of barium and bromate of baryta; evaporating the liquor to dryness, heating to redness, and treating with alcohol.

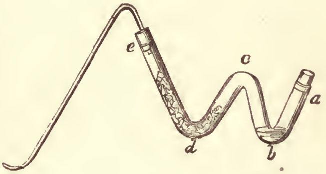
Properties. — Bromine condenses in the preceding process as a dense liquid under the water, the sp. gr. of bromine being 2.966. In mass, it is opaque and of a dark brown red, but in a thin stratum, transparent and of a hyacinth red. Its odour is powerful and very like that of chlorine. When cooled 10 or 15 degrees below zero, it freezes, and remains solid at 10°; it then has a leaden gray colour, and a lustre almost metallic. Bromine at the usual temperature is decidedly volatile, and to retard its evaporation it is generally covered by water in the bottle in which it is kept. It boils at 116°.5, and affords a vapour very similar to the ruddy fumes of peroxide of nitrogen. Bromine is soluble to a small extent in water, and gives an orange-coloured solution; it is more soluble in alcohol, and considerably more so in ether.

Bromine bleaches like chlorine, and acts in a similar manner upon the volatile oils and many organic substances containing hydrogen, which element it eliminates in the form of hydrobromic acid. Many metals combine with bromine with ignition, as they do with chlorine; it acts as a caustic on the skin, and stains it yellow, like nitric acid. It forms a compound with starch, which is of a yellow colour; like chlorine it forms a crystalline hydrate with water at 32°, which is of a beautiful red tint.

Hydrobromic acid; 79.26 *or* 990.8; HBr.—This is a gas, in which 2 volumes of each constituent are united without condensation, as in hydrochloric acid, and which has the great attraction for water of that acid. Hydrogen and bromine do not unite at the usual temperature, and a mixture of them is not exploded by flame, but they unite in contact with the flame and form hydrobromic acid. The same acid is more readily prepared by the action of bromine upon certain compounds of hydrogen, such as hydrosulphuric acid, phosphuretted hydrogen, and hydriodic acid. The gas may also be obtained by the mutual action of bromine, phosphorus, and water, and must be collected over mercury.

For the last process, a tube-apparatus, represented fig. 159, is recommended by M. Regnault. It contains a little bromine in the bend *b*, and small portions of phosphorus at *d*, this bend being filled up with fragments of glass, and a very minute quantity of water added. The open end *a* of the tube being closed with a cork, heat is applied to *b*, so as to vapourize the bromine in a gradual manner. A bromide of phosphorus is produced, which is immediately decomposed by the water, while hydrobromic acid is disengaged and escapes by the tube *e*.

Fig. 159.



Hydrobromic acid, like all the other bromides, is decomposed by chlorine, which is more powerful in its affinities than bromine, but it is not decomposed by iodine. Its action with metals is precisely similar to that of hydrochloric acid. Hydrobromic acid is not decomposed when heated with oxygen, and water is not decomposed by bromine, so that the affinity of bromine and oxygen for hydrogen may be inferred to be nearly equal. This acid, or a soluble bromide, produces white precipitates with the nitrates of silver, lead, and suboxide of mercury, which are very similar to the chlorides of these metals. The other metallic bromides correspond in solubility with the chlorides. The bromide of silver, like the chloride, is soluble in ammonia.

Bromic acid, BrO_5.—Bromine is dissolved by the strong alkaline bases, and occasions a decomposition exactly similar to that produced by chlorine, in which a bromide of the metal and bromate of the metallic oxide are formed. The bromic acid may be separated from bromate of baryta by sulphuric acid, and its solution may be concentrated to a certain point, like chloric acid, beyond which it undergoes decomposition. It has not been isolated. The chief points of difference between chloric and bromic acid are, that the latter alone is decomposed by sulphurous and phosphorous acids, and by hydrosulphuric acid; and while all the chlorates are soluble, the bromates of silver and suboxides of mercury are insoluble, the former being a white and the latter a yellowish white precipitate. Bromic acid is the only known oxide of bromine.

Chloride of bromine, $BrCl_5$.—Chlorine gas is absorbed by bromine, and a volatile fluid of a reddish yellow colour produced. This chloride appears to dissolve in water, without decomposition, but in an alkaline solution it is converted into chloride and bromate.

Bromide of sulphur.—Bromine combines when mixed with flowers of sulphur, forming a fluid of an oily appearance and reddish tint, much resembling subchloride of sulphur in appearance and properties. This bromide dissolves both sulphur and bromine, and has not been obtained in a state of sufficient purity for analysis.

Bromides of phosphorus, PBr_3 and PBr_5.—If bromine and phosphorus are brought into contact, in a flask filled with carbonic acid gas, a violent action with ignition takes place, of which the products are a volatile crystalline solid and a yel owish liquid. The former, when decomposed by water, affords hydrobromic and phosphoric acids, which proves it to be PBr_5; and the latter affords hydrochloric and phosphorous acids, which proves it to be PBr_3. The liquid bromide does not freeze at 5°, and, like the liquid chloride of phosphorus, is capable of dissolving a large quantity of phosphorus.

Bromide of silicon — Is prepared by a similar process as the chloride of silicon. It is a liquid boiling at 302°, and freezing at 10°. By water it is resolved into hydrobromic acid and silica.

[*See Supplement*, p. 795.]

SECTION XII.

IODINE.

Eq. 126.36 *or* 1579.5; I; *density of vapour* 8707; ◫

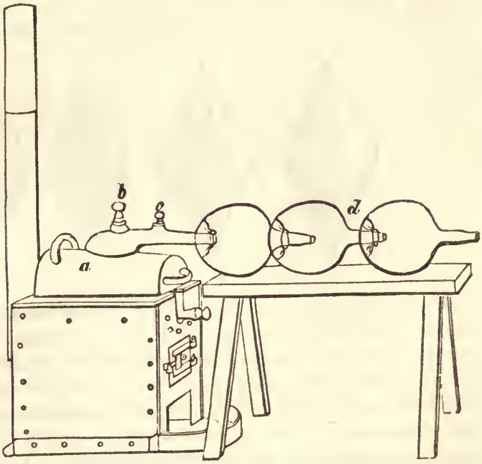
Iodine was discovered in 1811, by M. Courtois of Paris, in kelp, a substance from which he prepared carbonate of soda. Its chemical properties were examined by Clement, and afterwards, more completely, by Davy and Gay-Lussac, particularly by the latter (Davy, Phil. Trans. for 1814 aud 1815; Gay-Lussac, Annal. de Ch. lxxxviii., xc., et xci.) A trace of iodine has been observed in sea-water (Schweitzer), but it is more abundant in the fuci, ulvi, and other marine plants, and also in sponge, the ashes of which contain iodide of sodium. It is known also to exist in one mineral, a silver ore of Albaradon in Mexico. [*See Supplement*, p. 796.]

Preparation. — The greater part of the iodine of commerce is prepared at Glasgow from the kelp of the west coast of Ireland and western islands of Scotland. The seaweed thrown upon the beach is collected, dried, and afterwards burned in a shallow pit, in which the ashes accumulate and melt by the heat, being of a fusible material. The fused mass broken into lumps forms kelp, which was prepared and chiefly valued at one time for the carbonate of soda it contains, which varies in quantity from 2 to 5 per cent. It is not all equally rich in iodine. According to the observation of Mr. Whitelaw, the long elastic stems of the fucus palmatus afford most of the iodine contained in kelp, and the kelp prepared from this plant may be recognized by the presence of charred portions of the stems. This being a deep sea plant, iodine is found in largest quantity in the sea-wreck of exposed coasts. A high temperature in the preparation of the kelp, which increases the proportion of alkaline carbonate, diminishes that of the iodine, owing to the volatility of the iodide of sodium at a full red heat. The kelp which contains most iodine generally contains also most chloride of potassium, and it is for these two products that the substance is now valued, more than for its alkali.

The kelp broken into small pieces is lixiviated in water, to which it yields about half its weight of salts. The solution is evaporated down in an open pan, and when concentrated to a certain point, begins to deposit its soda salts, — namely, common salt, carbonate and sulphate of soda, — which are removed from the boiling liquor by means of a shovel pierced with holes like a colander. The liquid is afterwards run into a shallow pan to cool, in which it deposits a crop of crystals of chloride of potassium: the same operations are repeated upon the mother-ley of these crystals until it is exhausted. A dense dark-coloured liquid remains, which contains the iodide, in the form, it is believed, of iodide of sodium, but mixed with a large quantity of other salts; and this is called the iodine ley.

To this ley, sulphuric acid is gradually added in such quantity as to leave the liquid very sour, which causes an evolution of carbonic acid, sulphuretted hydrogen, and sulphurous acid gases, with a considerable deposition of sulphur. After standing for a day or two, the ley so prepared is heated with binoxide of manganese, to separate the iodine. This operation is conducted in a leaden retort *a* (see fig. 160) of a cylindrical form, supported in a sand-bath, which is heated by a small fire below.

Fig. 160.

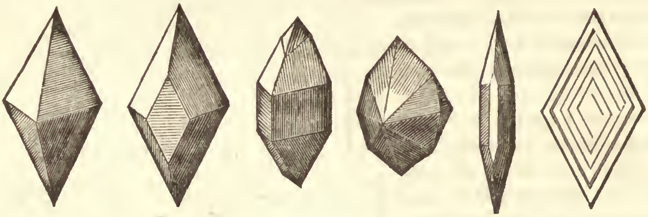


The retort has a large opening, to which a capital, *b c*, resembling the head of an alembic, is adapted, and luted with pipe-clay. In the capital itself there are two openings, a larger and a smaller, at *b* and *c*, closed by leaden stoppers. A series of bottles *d*, having each two openings, connected together as represented in the figure, and with their joinings luted, are used as condensers. The prepared ley being heated to about 140° in the retort, the manganese is then introduced, and *b c* luted to *a*. Iodine immediately begins to come off, and proceeds on to the condensers, in which it is collected; the progress of its evolution is watched by occasionally removing the stopper at *c*; and additions of sulphuric acid or manganese are made by *b*, if deemed necessary. The success of the experiment depends much upon its being slowly conducted, and upon the proper management of the temperature, which is more easily regulated when the quantities of materials are considerable, than when the experiment is attempted with small quantities in glass flasks. In the latter circumstances, chlorine is often evolved with the iodine, which escapes in acrid fumes, as the chloride of iodine, and is lost; but this accident can be avoided in the manufacturing process. A little cyanide of iodine often accompanies the iodine, which being more volatile, condenses in the form of white, flexible, prismatic crystals, in the bottle most distant from the leaden retort.

In this operation the binoxide of manganese will be in contact at once with hydriodic, hydrochloric, and sulphuric acids; and the iodine of the hydriodic acid may be liberated, from the union with its hydrogen of the oxygen of the manganese, and the formation of water; or hydrochloric acid may be first decomposed by the manganese, and chlorine decompose the hydriodic acid and liberate iodine. If a considerable excess of sulphuric acid be employed, iodine is obtained without the use of binoxide of manganese, the oxygen required by the hydrogen of the hydriodic acid being supplied by the sulphuric acid, a part of which is converted into sulphurous acid. The presence of iodine in the prepared ley may be observed by suddenly mixing it with an equal volume of oil of vitriol, when violet fumes of iodine appear. But the quantity of iodine may be more accurately estimated by means of a solution consisting of 1 part of crystallized sulphate of copper and $2\frac{1}{4}$ cr. protosulphate of iron, which throws down an insoluble subiodide of copper, almost white. It may also be determined approximatively by precipitation by the ammonio-nitrate of silver.

Properties.—Iodine is generally in crystalline scales of a bluish black colour and metallic lustre. It is obtained, from solution, in modifications of an elongated octohedron with rhomboidal base (fig. 161.) The density of iodine is 4·948; it fuses at 225°, and boils at 347°; but it evaporates at the usual temperature, and more rapidly when damp than when dry, diffusing an odour having considerable resemblance to chlorine, but easily distinguished from it. Iodine stains the skin of a yellow colour, which however disappears in a few hours. Its vapour is of a splendid violet colour, which is seen to great advantage when a scruple or two of iodine is thrown at once upon a hot brick. Hence its name, from Ἰώδης, violet-coloured. The vapour of iodine is one of the heaviest of gaseous bodies, its density being 8716 according to the experiment of Dumas, and 8707.7 according to calculation from its atomic weight.

FIG. 161.



Pure water dissolves about 1-7000th of its weight of iodine, and acquires a brown colour; but when charged with salt, particularly the nitrate or hydrochlorate of ammonia, water dissolves a considerably greater quantity of iodine. The solution of iodine does not disengage oxygen in the light of the sun, and does not destroy vegetable colours, but after a time it becomes colourless, and then contains hydriodic and iodic acids. In other respects, iodine generally comports itself like chlorine, but its affinities are much less powerful. Iodine is soluble in alcohol and ether, with which it forms dark reddish-brown liquids. Solutions of iodides, too, all dissolve much iodine, and become of a deep red colour. A liquid containing 20 grains of iodine and 30 grains of iodide of potassium in 1 ounce of water, is known as Lugol's solution, and preferred to the tincture in medicine, because the iodine is not precipitated from it by dilution with water.

A solution of starch forms a compound with iodine, of a deep blue colour, soluble in pure water but insoluble in acid and saline solutions, the production of which is an exceedingly delicate test of iodine. If the iodine be free, starch produces at once the blue compound, but if the iodine be in combination as a soluble iodide, no change takes place till chlorine is added to liberate the iodine. If more chlorine, however, be added than is necessary for that purpose, the iodine is withdrawn from the starch, chloride of iodine formed, and the blue compound destroyed. Dr. A. T. Thomson, after adding the starch with a drop of sulphuric acid to the liquid containing an iodide, in a cylindrical vessel, allows the vapour only from the chlorine-water bottle to fall upon the solution, and not the chlorine-water itself. In this way, the danger of adding an excess of chlorine is easily avoided, and the test indicates in a sensible manner an exceedingly minute quantity of iodine. The iodide of starch, in water, becomes colourless when heated, but recovers its blue colour if immediately cooled. The soluble iodides give, with the nitrate of silver, an insoluble iodide of silver, of a pale yellow colour, insoluble in ammonia; with salts of lead, an iodide of a rich yellow colour, and with corrosive sublimate, a fine scarlet iodide of mercury.

In ascertaining the quantity of iodine in the mixed chlorides, and iodides of mineral waters and other solutions, Rose recommends the addition of nitrate of silver, which throws down a mixture of chloride and iodide of silver, which is fused and weighed. This is afterwards heated in a tube and chlorine passed over it, by which the iodine is expelled, and the whole becomes chloride of silver. It is weighed again, and a loss is found to have occurred, owing to the equivalent of the replacing chlorine being less than that of the replaced iodine. This loss, multiplied by 1·389, gives the quantity of iodine originally present, which has been expelled by the chlorine. (Handbuch der analyt. Chem. von Heinrich Rose, B. 2, p. 577). Dr. Schweitzer employs a similar method in estimating the quantity of iodine when mixed with bromine, heating the iodide and bromide of silver in an atmosphere of bromine. The difference of weight multiplied by 2.627 gives the proportion of iodine, and multiplied by 1.627 the proportion of bromine. (Phil. Mag., 3d series, xv. p. 57.)

Uses.—Iodine is employed in the laboratory for many chemical preparations, and as a test of starch. It was first introduced into medicine by Coindet of Geneva, who employed it with success, in the treatment of goitre, dissolved in alcohol, in solution of iodide of potassium, or as iodide of sodium; and since that application, most mineral waters to which the virtue of curing goitre was ascribed, have been found to contain iodine. M. Boussingault has adduced striking confirmations of the efficacy of iodine in that disease, in his interesting memoir on the iodiferous mineral waters of the Andes. (Annal. de Chim. et de Phys., liv. 163.) It appears to have a specific action in causing the absorption of glandular swellings, and is also administered as a tonic. Iodine swallowed in the solid state causes ulceration of the mucous membrane of the stomach, and death. But the iodide of potassium or sodium is not poisonous in considerable doses, nor is the iodide of starch hurtful (Dr. A. Buchanan). Iodine and bromine have also found an interesting application to form the film of iodide or bromide of silver, in the silver-plates of the daguerreotype, which is so sensitive to light.

Iodides.—Iodine does not form a hydrate like chlorine, but it combines with another compound body, ammonia; dry iodine absorbing dry ammoniacal gas and running into a brown liquid, which Bineau found to contain 20.4 ammonia to 100 iodine, quantities in the proportion of 3 equivalents of ammonia to 2 of iodine. (Annal. de Chim. et de Phys., lxvii. 226.) This liquid dissolves iodine. Iodine does not combine with dry iodide of potassium, but with the addition of a small quantity of water, it forms what appears to be a ternary compound of iodide of potassium, water and iodine, which is usually fluid, but was obtained in crystals by Bauer. Iodine forms similar compounds with other hydrated metallic iodides. With the metals generally iodine combines, with the same facility, and nearly with as much energy as chlorine does. The iodide of zinc and protiodide of iron, which are very soluble, are formed by simply bringing the metals into contact with iodine, in water. All the iodides are decomposed by bromine, as well as by chlorine.

The compounds of iodine may be shortly described in the following order:—

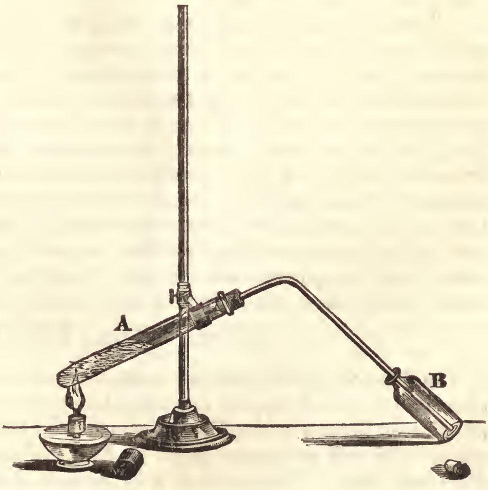
Hydriodic acid .... HI
*Iodic acid .... IO_5
Periodic acid .... IO_7
Iodide of nitrogen ... NI_3

Iodide of sulphur
Iodides of phosphorus
Chlorides of iodine
Bromides of iodine.

COMPOUNDS OF IODINE.

Hydriodic acid; 127.36 *or* 1592; HI.—Hydriodic acid cannot be prepared with advantage by treating the iodide of sodium or potassium with hydrated sulphuric acid, as the latter is partially converted into sulphurous acid by hydriodic acid, with the separation of iodine. It may be obtained in the state of gas, by forming an iodide of phosphorus, 9 parts of dry iodine and 1 of phosphorus being introduced into a tube sealed at one end, to be used as a retort, and the mixture covered by pounded glass, and combination determined by a gentle heat; and afterwards decomposing this iodide of phos-

FIG. 162.



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* [*See Supplement*, p. 796.]

phorus by a few drops of water. Hydriodic acid instantly comes off as gas, and hydrated phosphorous acid remains in the tube:

$$PI_3 \text{ and } 6HO = 3HI \text{ and } 3HO + PO_3.$$

A slight heat may be applied to the tube, when the action abates, to expel the last portions of hydriodic acid; but if the temperature be elevated, the residuary hydrated phosphorous acid is decomposed, with evolution of phosphuretted hydrogen gas, which may, therefore, be obtained by the same operation. This gas is very soluble in water, and soon decomposed over mercury, which combines with its iodine and liberates hydrogen; so that it is collected in a dry bottle, B, by the method of displacement, and the bottle is closed with a glass stopper when full of gas. Hydriodic gas is colourless, of density 4443 by experiment and 4385 by theory, and consists of 2 volumes of iodine vapour and 2 volumes of hydrogen gas united without condensation, or forming 4 volumes, which are, therefore, the combining measure of the gas. In the combination of its constituents by volume, hydriodic acid resembles hydrochloric acid gas and all the other hydrogen acids. Hydriodic acid gas is gradually decomposed by oxygen, with the formation of water: iodine is liberated.

The solution of this acid in water may be obtained by transmitting hydrosulphuric acid gas through water in which iodine is suspended: the iodine combines with the hydrogen of that compound and liberates the sulphur. The liquid may afterwards be warmed to expel the excess of hydrosulphuric acid, and filtered. It is colourless at first, but in a few hours becomes red, owing to the decomposition of hydriodic acid by the oxygen of the air, and solution of the iodine in the acid.

The solution has its maximum boiling point, which lies between 257° and 262°, when of sp. gr. 1.7, according to Gay-Lussac. Nitric and sulphuric acids decompose it, and are decomposed themselves with the formation of water; the starch test then indicates free iodine.

Iodic acid; 166.36 *or* 2079.5; IO_5. — Iodine does not afford a peculiar acid compound with red oxide of mercury and those metallic oxides which yield free hypochlorous acid with chlorine. Nor is it absorbed, like chlorine, by hydrate of lime or alkaline solutions, to form a class of bleaching salts. Such compounds are wanting in the series of oxides of iodine, which is limited to hypoiodic, iodic, and periodic acids. Sementini imagined that he had formed inferior oxides of iodine, but he is evidently mistaken. The iodate of soda combines with iodide of sodium in several proportions, one of which was supposed by Mitscherlich, when he discovered it, to be an iodite of soda; but that this is a double salt of the constitution first mentioned is more probable.

A few grains of iodic acid may easily be prepared by the method of Mr. Connel, which consists in heating the most concentrated nitric acid, free from nitrous vapour, upon a little iodine, in a wide glass tube, and allowing the liquid to cool; the iodine is oxidated at the expense of the nitric acid, and the greater part of the iodic acid is deposited in crystals. When a larger quantity is required, a convenient process is to form, in the first place, an iodate of soda, as suggested by Liebig. An ounce or two of iodine in powder may be suspended in a pound of water, with occasional agitation, and a stream of chlorine be passed through till the whole iodine is dissolved. Carbonate of soda is then added to the liquid, which is of a brown colour and strongly acid, till it becomes slightly alkaline, when a large precipitation of iodine occurs, which may be separated and collected on a filter. This iodine may be suspended in water, and exposed to a stream of chlorine as before.

$$5Cl \text{ and } 5HO \text{ and } I = 5HCl \text{ and } IO_5.$$

The filtered solution contains iodate of soda and chloride of sodium, with a trace of carbonate, which may be neutralized by hydrochloric acid. On afterwards adding chloride of barium to the filtered solution, so long as a precipitate is produced, the whole iodic acid is thrown down as iodate of baryta, which may be collected on a filter and dried. This iodate is anhydrous, and may be decomposed completely, by boiling 9 parts of it for half an hour with 2 parts of oil of vitriol, diluted with 10 or 12 parts of water. The liberated iodic acid dissolves, and being separated from the sulphate of baryta by filtration, is obtained as a crystalline mass when evaporated to dryness by a gentle heat.

This acid is also prepared very easily, according to M. Millon, by digesting iodine in a mixture of nitric acid and chlorate of potassa; the proportions recommended are 4 of iodine, 7.5 chlorate of potassa, 10 of nitric acid, and 40 of water. The iodic acid is afterwards precipitated in the form of iodate of baryta, as in the preceding process, the iodate of baryta then decomposed by sulphuric acid.

Iodic acid crystallizes from a strong solution, as a hydrate, $HO.IO_5$, in large and transparent crystals, which are six-sided tables. This acid is not sublimed, but decomposed into iodine and oxygen, by a high temperature, without any formation of periodic acid. Another definite hydrate of iodic acid was obtained by M. Millon, containing only one-third of an equivalent of water, by maintaining the protohydrate at a temperature of 266° (130° C.), so long as it continued to lose weight. It is also formed when the protohydrate is mixed with an excess of anhydrous alcohol. By drying either of these hydrates at 338° (170° C.), iodic acid is obtained entirely anhydrous (IO_5).

Iodic acid is very soluble in water; and after reddening, bleaches litmus paper. It oxidates all metals with which it has been tried, except gold and platinum. It is deoxidized by sulphurous acid and hydrosulphuric acid, and iodine liberated, but an excess of sulphurous acid causes the iodine again to disappear as hydriodic acid, water being decomposed by the simultaneous action of sulphurous acid and iodine upon its elements. Iodic acid is easily decomposed by heat, disengaging oxygen and vapours of iodine. It is soluble in water, alcohol, and ether.

Iodates.—The salts of iodic acid have a general resemblance to chlorates; when thrown upon burning embers they enliven the combustion, but with less vivacity than chlorates. The iodate of potassa is converted by heat into iodide of potassium and oxygen; so that the composition of iodic acid may be determined from that of iodate of potassa, in the same manner as the composition of chloric acid is determined from that of chlorate of potassa. The iodate of soda, however, loses iodine as well as oxygen, when heated, and a yellow, sparingly soluble, alkaline matter remains, which Liebig supposes to contain the salt of an iodous acid, resolvable into an iodate and iodide by solution in water, but which requires further investigation. The iodates of metallic protoxides, with the exception of the potassa family, are all sparingly soluble or insoluble salts. The iodate of lime contains water, and when heated affords no iodide of calcium, but caustic lime.

Fixed acids, which have little affinity for water, such as iodic acid, appear often to combine in several proportions with oxides of the potassa family. The ordinary biniodate of potassa contains 1 eq. of basic water, but at a high temperature it is made anhydrous, and then a salt remains containing 2 eq. of acid to 1 of potassa. Mr. Penny has crystallized a biniodate and teriodate of soda, both anhydrous.

Iodic acid likewise combines with other acids. These compounds generally precipitate in a crystalline form, when another acid is added to a hot and concentrated solution of iodic acid. Compounds of sulphuric, nitric, phosphoric, and boracic acids, with iodic acid, have been formed. It has been observed by M. Millon, that when the compound with sulphuric acid is submitted to heat, oxygen is evolved, and a hypoiodic acid or peroxide of iodine formed, of which the formula is IO_4. There is formed besides in this decomposition, according to M. Millon, a peculiar double acid, which may be considered a compound of iodous and hypo-iodic acid, having for formula $4IO_4+IO_3$. When vegetable acids are dissolved in iodic acid, they are immediately decomposed by it, carbonic acid being disengaged with effervescence, and iodine precipitated.

Periodic acid, Hyperiodic acid; 182.36 *or* 2279.5; IO_7.—This acid, which was discovered by Magnus and Ammermuller, is formed by transmitting a current of chlorine through a solution of iodate of soda, to which a portion of carbonate is added, and the whole maintained in constant ebullition. On allowing the solution to cool, a basic periodate of soda is deposited in tufts of silky crystals, and the chloride of sodium, formed at the same time, retained in solution. This basic periodate of soda, which is almost insoluble in cold water, is dissolved in nitric acid, and nitrate of silver added, which throws down a basic periodate of silver, also of sparing solubility. The last salt may be washed, and afterwards dissolved in boiling nitric acid, and the solution on cooling yields orange-yellow crystals of neutral periodate of silver. It is remarkable that when these crystals are thrown into water they are decomposed, the whole oxide of silver precipitating with half the periodic acid, as the former basic periodate, while half of the acid is dissolved by the water without a trace of silver, and obtained in a state of purity. This solution when evaporated affords periodic acid in crystals, which are unalterable in the air, and of which the solution in water is not changed by ebullition. The crystals fuse about 266° (130° C.) The solution, treated with hydrochloric acid, affords chlorine and iodic acid, water being formed. Periodic acid is resolved into oxygen and iodine by a high temperature.

Periodates.—Besides neutral salts of this acid, subsalts of the potassa family exist which contain two of base to one of acid. The sparing solubility of the basic salt of soda is the most remarkable character of periodic acid. True subsalts of the potassa family are so extremely unusual, that it is more probable that periodic acid forms a second and bibasic class of salts, to which they belong. (Poggendorff's Annalen, xxviii. 514). The periodates are decomposed by heat like the iodates, but yield more oxygen.

Iodide of nitrogen.—Dry iodine and ammonia unite directly, and form a brown liquid, of which the formula is $3(H_3N).I_2$. But when digested in the solution of ammonia, iodine acts upon that substance as chlorine does, and forms an insoluble black powder, which is powerfully detonating, and analogous to the chloride of nitrogen. The iodide detonates more easily, but less violently, than the chloride, always exploding spontaneously when it dries. Another process is to mix a great excess of ammonia with a saturated solution of iodine in alcohol, and afterwards to add water so long as iodide of nitrogen precipitates. The filter with the humid precipitate should be divided into several pieces, otherwise the whole may explode at once upon drying. [*See Supplement*, p. 797.]

Although named the iodide of nitrogen, this substance contains hydrogen as a constituent, according to the observations of M. Bineau, and may be represented by I_2HN; or ammonia in which 2 eqs. of hydrogen are replaced by 2 eqs. of iodine. The same substance is represented by Millon, as $I_3N + 2H_3N$.

When caustic soda is added to the solution of iodine in alcohol or wood-spirit, a yellow substance of a saffron odour precipitates, which was supposed at one time to be the periodide of carbon, but is really *iodoform*, of which the formula is C_2HI_3. No true iodide of carbon is known.

Iodide of sulphur.—This compound is formed by fusing together 4 parts of iodine and one of sulphur. It has a radiated crystalline structure, but its elements are easily disunited, the iodine escaping entirely from this compound when it is left exposed in the air.

Iodides of phosphorus.—Iodine appears to combine with phosphorus in several proportions, when they are brought in contact and slightly heated. In all these combinations the mass becomes hot without inflaming, if the phosphorus is not at the same time in contact with air. One part of phosphorus with 6, 12, and 20 parts of iodine, forms fusible solids, which may be sublimed without change, but which are decomposed by water, all of them yielding hydriodic acid, and the first affording, besides, phosphorus and phosphorous acid, the second phosphorous acid, and the third phosphoric acid. [*See Supplement*, p. 798.]

Chlorides of iodine.—Chlorine is readily absorbed by dry iodine; when the latter is in excess, a protochloride, ICl, appears to be formed; and when the chlorine is in excess, a terchloride, ICl_3.

Berzelius produced the protochloride by distilling a mixture of 1 part of iodine with 4 parts or more of chlorate of potassa. There is formed in the retort a mixture of iodate and perchlorate of potassa, at the same time that oxygen gas is disengaged, and the chloride of iodine is produced, which condenses in the receiver. This compound is a yellow or reddish liquid, of an oily consistence, of a sharp and peculiar odour, and taste which is feebly acid, but very astringent and rough. It is soluble in water and alcohol; and ether extracts it from its aqueous solution unaltered, so that it is not decomposed by water.

When iodine is saturated with chlorine, it forms a compound which is solid and crystallizable, and of a yellow colour; fusible by heat, but which cannot be sublimed without loss of chlorine. It fumes in air, and has an acrid odour. When this terchloride of iodine is dissolved in water, and the solution saturated with carbonate of soda, chloride of sodium is formed, and some iodate of soda; while at the same time a large quantity of iodine precipitates. By the continued action of chlorine upon iodine in a considerable quantity of water, the liquid becomes at last entirely colourless, and then contains nothing but hydrochloric and iodic acids.

Bromides of iodine.—Iodine likewise forms two bromides, which are both soluble in water. The solution bleaches litmus paper without first reddening it.

SECTION XIII.

FLUORINE.

Eq. 18.70 *or* 233.8; F; *density* (*hypothetical*) 1292; ☐☐

This elementary body is most frequently found in the mineral kingdom in combination with calcium, as fluoride of calcium, which constitutes the mineral fluor-spar; it exists in small quantity in amphibole, mica, and most of the natural phosphates: a trace of it also occurs in the enamel of the teeth, and in the bones of animals. Of all bodies, fluorine appears to possess the most powerful and general affinities, and to be, therefore, the most difficult to isolate and preserve for the study of its properties. Indeed, we have hitherto learned little more of fluorine than that it exists and may be isolated. Several of its compounds, however, are of less difficult preparation, and well known. [*See Supplement*, p. 800.]

Sir H. Davy made several attempts to isolate fluorine. He exposed the fluoride of silver in a glass tube to gaseous chlorine, at a high temperature, and found that chloride of silver was produced, and fluorine therefore liberated; but it was absorbed and replaced by oxygen, which it disengaged from the silica and soda of the glass. When Davy repeated the same experiment in a platinum vessel, the metal became covered with fluoride of platinum. He proposed afterwards to construct vessels of fluor-spar for the reception of the fluorine, which he expected to disengage from the fluoride of phosphorus by burning it in oxygen gas; but he does not appear to have carried this project into execution. The Messrs. Knox and M. Louyet have announced that they have separated fluorine from the fluorides of silver and mercury, by treating these bodies with chlorine or iodine in vessels of fluor-spar, when fluorine was disengaged in the form of a colourless gas. Gold and platinum did not appear to be acted upon by fluorine, except when it was in the nascent state.

No compound of fluorine and oxygen is yet known, but a compound of fluorine and hydrogen is easily formed, and is of importance from its applications.

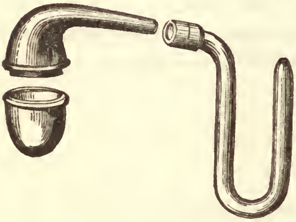
HYDROFLUORIC ACID.

Eq. 19.7 *or* 246.3; HF.

Schwankhardt, of Nuremberg, observed in 1670, that it was possible to etch upon glass by means of fluor-spar and sulphuric acid, but it was not till 1771 that Scheele referred this action to a particular acid which sulphuric acid disengaged from fluor-spar. Wenzel first obtained the true hydrofluoric acid, exempt from silica, by preparing it in proper metallic vessels; the acid collected by Scheele being the fluosilicic, and not the hydrofluoric. The preparation and properties of the pure acid were more fully studied by Gay-Lussac and Thénard in 1810. It was then known as fluoric acid, and was supposed, according to the doctrine of the day, to contain oxygen. The idea of its being a hydrogen acid was first suggested, a few years afterwards, by M. Ampère, whose views in theoretical chemistry were often marked by much acuteness and originality. The view of Ampère was generally assented to, and is confirmed by the isomorphism of the fluorides with the chlorides, bromides, and iodides, observed by M. Louyet.

Preparation. — To obtain hydrofluoric acid, a specimen of fluor-spar is selected, free from silicious minerals and galena; this is reduced to an impalpable powder, and distilled in a retort of lead (fig. 163), by a gentle heat, such as that of an oil-bath, with twice its weight of highly concentrated oil of vitriol. The materials become viscid and swell considerably, and an acid vapour distils over, which is even more acrid and suffocating than chlorine, and produces severe sores if allowed to condense upon the hands of the operator. This vapour is received in a bent tube, likewise of lead, used as a receiver, and kept cold by a freezing mixture, in which the hydrofluoric acid condenses without the presence of water. The acid thus obtained may be preserved in vessels of platinum or gold, provided with stoppers of the same metal which fit accurately; or in vessels of lead formed without tin solder, tin being rapidly acted upon by hydrofluoric acid. If a dilute solution of this acid in water is required, the extremity of the leaden tube, from the retort, may be allowed to touch the surface of water in a platinum crucible or capsule, by which the acid vapour is readily condensed; and the dilute acid may be preserved, without much contamination, in a glass bottle which has been previously heated, and coated internally with melted bees'-wax.

Fig. 163.



Fluor-spar, which is employed in this operation, is the fluoride of calcium, upon which the action of hydrated sulphuric acid is similar to its action upon chloride of sodium, when hydrochloric acid is produced. Water is decomposed, by the hydrogen and oxygen of which the fluorine and calcium are converted respectively into hydrofluoric acid and lime, the former coming off as vapour, while the latter remains in the retort as sulphate of lime. In symbols—

$$\text{CaF and HO.SO}_3 = \text{HF and CaO.SO}_3.$$

Properties.—The acid liquid obtained by the preceding process, which has hitherto been considered as the anhydrous acid, is, according to M. Louyet, a hydrate. Distilled with anhydrous phosphoric acid, it loses water, and gives rise to a colourless gas, fuming in air like hydrochloric acid, which is the true anhydrous hydrofluoric acid. M. Louyet finds this gaseous acid to have no sensible action upon dry glass.

The former product is a colourless, fuming, and very volatile liquid, boiling not much above 60°; and which does not freeze at 4°. Its sp. gr., which is 1.0609, is increased to 1.25 by the addition of a certain quantity of water, for which it has an intense affinity. Hydrofluoric, like hydrochloric acid, dissolves the more oxidable metals with the evolution of hydrogen gas. Mixed with nitric acid, it dissolves ignited silicon and titanium, with disengagement of nitric oxide; but that acid mixture has no action upon the nobler metals, such as gold and platinum, which are dissolved by aqua regia. Several insoluble acid bodies, which are not acted on by sulphuric, nitric, or hydrochloric acid, are dissolved with facility by hydrofluoric acid; such as silica, titanic, tantalic, molybdic and tungstic acids. Water is then formed from the oxygen of these acids and the hydrogen of hydrofluoric acid, and fluorides of silicon or of the metals of the acids enumerated are likewise produced; which fluorides appear to combine with undecomposed hydrofluoric acid, when water is present. This acid destroys glass by acting upon its silica. If a drop of the concentrated acid be allowed to fall upon a glass plate, it becomes hot, enters into ebullition and volatilizes in a thick smoke, leaving the spot with which it was in contact deeply corroded, and covered by a white powder composed of the elements of the glass, excepting a portion of the silica, which has passed off as gaseous fluoride of silicon.

The diluted solution, or the vapour of hydrofluoric acid, is sometimes used to etch upon glass. The purity of the acid being of little moment in this application of it, the sulphuric acid and fluor-spar may be mixed in a stone-ware evaporating basin. The glass is warmed sufficiently to melt bees'-wax rubbed upon it, and thereby covered with a coating of that substance, which is afterwards removed from the parts to be etched, by a pointed rod of lead or tin, employed as a graver. A gentle heat being applied to the basin, acid fumes are evolved, to which the etched surface of the glass is exposed for a minute or two, care being taken not to melt the wax. The wax is afterwards removed by warming the glass, and wiping it with tow and a little oil of turpentine, when the exposed lines are found engraved to a depth proportional to the time they have been exposed to the acid fumes. But in taking impressions upon paper from glass plates engraved in this way, as from a copper-plate, they are too apt to be broken from the pressure applied in printing.

To discover the minute quantity of hydrofluoric acid which exists in many minerals, Berzelius recommends that the substance to be examined be reduced to fine powder and mixed with concentrated sulphuric acid, in a platinum crucible covered by a small plate of glass, waxed and engraved as described. The crucible is then exposed to a gentle heat, insufficient to melt the wax, and, in half an hour, the glass plate may be removed and cleaned. If the mineral submitted to the test contains fluorine, the design will be perceived upon the glass; when the quantity of fluorine, however, is very small, the engraving does not appear immediately, but becomes visible on passing the breath over the glass. The presence of silica in the mineral interferes with this operation, but an indication may then be obtained by heating a fragment of the mineral to redness upon a piece of platinum foil slipped into a glass tube, 8 or 10 inches in length, and open at both ends. The tube is held obliquely with the mineral near the lower end, and so that part of the vapour from the flame passes up the tube. The moisture thus introduced carries away the gaseous fluoride of silicon, and condenses in drops in the upper part of the tube. These drops, when afterwards evaporated, in drying the tube, leave a white spot, which consists of silica, resulting from the decomposition of the fluoride of silicon by the water with which it condensed. (Berzelius).

Fluoride of boron, fluoboric acid; 67·0 *or* 837·5; BF_3.—This compound is gaseous, and is obtained when dry boracic acid is brought in contact with concentrated hydrofluoric acid; when boracic acid is ignited with fluor spar; and most conveniently by heating together in a glass retort, 1 part of vitrified boracic acid in fine powder, 2 of fluor spar, and 12 of concentrated sulphuric acid, although this process does not give it free from fluosilicic acid. The reaction by which the fluoboric acid is then produced may be thus expressed:—

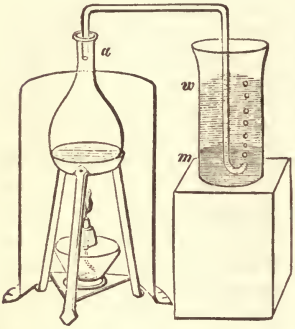
$$3CaF \text{ and } BO_3 \text{ and } 3(HO.SO_3) = 3(CaO.SO_3) \text{ and } 3HO \text{ and } BF_3.$$

Fluoboric acid gas has no action upon glass, and may be collected in glass vessels over mercury. It is colourless, but produces thick fumes when allowed to escape into the atmosphere. Its density, according to Dr. J. Davy, is 2371, and 2312 according to Dumas, who finds 1 volume of this gas to contain $1\frac{1}{2}$ vol. of fluorine. Fluoboric gas is not decomposed by iron and the ordinary metals, even at a bright red heat, but on the contrary, potassium, with the metals of the alkalies and alkaline earths, decomposes it at a red heat; boron is liberated by potassium, and a double fluoride of boron and potassium also formed. Water absorbs fluoboric acid gas with the greatest avidity, taking up, according to J. Davy, 700 times its volume, which increases its bulk considerably, and raises its density to 1.77. Sulphuric acid can dissolve 50 times its volume of the fluoride of boron. The most ready mode of preparing the aqueous solution of this acid is to dissolve crystallized boracic acid in hydrofluoric acid. The acid is extremely caustic and corrosive, charring and destroying wood and organic matters, when concentrated, like sulphuric acid, probably from its avidity for moisture.

A dilute solution of fluoride of boron undergoes spontaneous decomposition, according to Berzelius, depositing one-fourth of its boron in the form of boracic acid, which crystallizes at a low temperature; while a compound of hydrofluoric acid and fluoride of boron remains in solution, which he termed *hydrofluoboric acid.* The fluoride of boron has a great disposition to form double fluorides, and acts upon basic metallic oxides like the following compound.

Fluoride of silicon, fluosilicic acid; 77.45 *or* 968.12; SiF_3.—This gas is obtained in the following manner:—Equal parts of fluor spar and broken glass or quartzy sand, in fine powder, are mixed in a glass flask *a* (fig. 164), to be used as a retort, with six parts of concentrated sulphuric acid, and stirred well together. A disengagement of gas immediately takes place, and the mass swells up considerably. After a time, a gentle heat is required to aid the operation. Fluosilicic gas is collected over mercury. In its physical characters it resembles fluoboric gas. It is colourless and fumes in air; it extinguishes bodies in combustion, and does not attack glass. Its density is 3574 according to J. Davy, and 3600 according to Dumas; it contains twice its volume of fluorine.

Fig. 164.



In transmitting this gas into water, the tube must not dip in the fluid, for it would speedily be choked by the deposition of silica produced by the action of water upon the gas. In the arrangement figured, the extremity of the exit tube is covered by a small column of mercury *m*, in the lower part of the jar, through which the gas passes before it reaches the water *w*. Every bubble of gas exhibits a remarkable phenomenon, as it enters the water, becoming invested with a white bag of silica, which rises to the surface. It often happens, in the course of the operation, that the gas forms tubes of silica in the water, through which it gains the surface without decomposition, if they are not broken from time to time. When water is completely saturated with the fluoride of silicon, it has taken up about once and a half its weight, and is a gelatinous, semi-transparent mass, which fumes in the air. The liquid contains two equivalents of water to one of the original fluoride of silicon: but one-third of the fluoride has been decomposed by the water and converted into hydrofluoric acid and silica. The hydrofluoric acid and fluoride of silicon, in solution, were supposed to be in combination by Berzelius, forming $3HF + 2SiF_3$, which was termed by him *hydrofluosilicic* acid. When this liquid is placed in a moderately warm situation, the whole of it gradually evaporates; the free hydrofluoric acid reacting upon the deposited silica, with formation of water, and fluoride of silicon being revived.

The most remarkable property of the fluoride of silicon is to produce, with neutral salts of potassa, soda and lithia, precipitates which are gelatinous, and so transparent as to be scarcely visible at first in the liquid; and with salts of baryta, a white and crystalline precipitate, which appears in a few seconds. It is often employed to decompose a salt of potassa, for the purpose of isolating its acid. It also serves to distinguish salts of baryta from salts of strontia; the salts of baryta producing with this acid a salt scarcely soluble in water, while the salts of strontia are not precipitated.

Almost all the basic metallic oxides decompose this acid, when they are employed in excess, separating silica, and giving rise to metallic fluorides. When, on the other hand, no more of the base is applied than the quantity required to neutralize the free hydrofluoric acid, combinations are obtained with all bases, which are analogous to double salts; consisting of a metallic fluoride combined with fluoride of silicon, the proportion of the latter containing twice as much fluorine as the former. The formula of one of these compounds, the double fluoride of silicon and potassium, is $2SiF_3 + 3KF$; and those of other metals are similar. The ratio of 2 to 3, in the equivalents of the two fluorides which form these double salts, is unusual. But the double fluorides in question may be represented by single equivalents of fluoride of silicon and metallic fluoride, as was suggested by Dr. Clark, by adopting the low equivalent of silicon 12.6, when silica is made to consist of 1 equivalent of silicon and 2 equivalents of oxygen, and the fluoride of silicon of 1 equivalent of silicon and 2 equivalents of fluorine.

CHAPTER VI.

METALLIC ELEMENTS.

GENERAL OBSERVATIONS.

The metallic class of elements is considerably more numerous than the non-metallic class, embracing forty-eight elementary bodies. Of these seven only were known to the ancients, and of the remainder, a large proportion are of recent discovery. Their names and their densities, when accurately determined, with the dates and authors of their discovery, are contained in the following table, compiled chiefly from the work of Dr. Turner:—

Table of Metals.

Name.	Density.	Dates and Authors of the Discovery.
Gold	19·257 Brisson, to 19·361	Known to the Ancients.
Silver	10·474, ditto	
Iron	7·778, ditto	
Copper	8·895, Hatchett	
Mercury	13·596, at 32° Regnault	
Lead	11·352, Brisson	
Tin	7·291, ditto	
Antimony	6·702, ditto	1490, described by Basil Valentine.
Bismuth	9·822, ditto	1530, described by Agricola.
Zinc	6·861 to 7·1, ditto	16th century, first mentioned by Paracelsus.
Arsenic	5·884, Turner	1733, Brandt.
Cobalt	8·538, Haüy	
Platinum	20·336 Brisson, to 22·069	1741, Wood, assay-master, Jamaica.
Nickel	8·279, Richter	1751, Cronstedt.
Manganese	7·500	1774, Gahn and Scheele.
Tungsten	17·6, D'Elhuyart	1781, D'Elhuyart.
Tellurium	6·115, Klaproth	1782, Müller.
Molybdenum	7·400, Hielm	1782, Hielm.
Uranium	9·000, Bucholz	1789, Klaproth.
Titanium	5·3, Wollaston	1791, Gregor.
Chromium	5·9,	1797, Vauquelin.
Tantalum		1802, Hatchett.

Table of Metals — continued.

Name.	Density.	Dates and Authors of the Discovery.
Palladium	11·3 to 11·8, Wollaston	1803, Wollaston.
Rhodium	10·649	
Iridium	18·680, [21·8, Hare]	1803, Descotils and Smithson Tennant.
Osmium	10·0	1803, Smithson Tennant.
Cerium		1804, Hisinger and Berzelius.
Potassium	0·865 Gay Lussac and Thénard	1807, Davy.
Sodium	0·972 Gay Lussac and Thénard	
Barium		
Strontium		
Calcium		
Cadmium	8·604, Stromeyer	1818, Stromeyer.
Lithium		1818, Arfwedson.
Zirconium		1824, Berzelius.
Aluminum		1828, Wöhler.
Glucinum		
Yttrium		
Thorium		1829, Berzelius.
Magnesium		1829, Bussy.
Vanadium		1830, Sefström.
Lantanum		1839, Mosander.
Didymium		Since 1840, Mosander.
Erbium		
Terbium		
Ruthenium		1844, Klaus.
Pelopium		1845, H. Rose.
Niobium		

Of the physical properties of metals and their combinations with each other, the most characteristic is their lustre and power to reflect much of the light which falls upon them, — a property exhibited in a high degree by burnished steel, speculum metal, and the reflecting surface of mercury in glass mirrors. Metals are also remarkable for their opacity, although they have a certain degree of transparency in a highly attenuated state, as fine gold-leaf allows light of a green colour to pass through it. They are peculiarly the conductors of electricity, and also the best conductors of heat. The most dense substances in nature are found among the metals, — gold, for instance, being upwards of nineteen, and laminated platinum twenty-two times heavier than an equal bulk of water. But some of the metals, notwithstanding, are very light, potassium and sodium floating upon the surface of water.

Certain metals possess a valuable property, *malleability*, depending upon a high tenacity with a certain degree of softness; particularly gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and solid mercury. These metals may all be hammered out into plates, or even into thin leaves. In zinc this property is found in the highest degree between 300° and 400°, and in iron at a degree of temperature exceeding a red heat. The same metals are likewise *ductile*, or may be drawn into wires, although the ductility of different metals is not always proportional to their malleability, iron being highly ductile, although it cannot be beaten into very thin leaves. By a peculiar method, Dr. Wollaston formed gold wire so small that it was only 1-5000th of an inch in diameter, and 550 feet of it were required to weigh one grain. He also obtained a wire of platinum not more than 1-30,000th of an inch in diameter, (Phil. Trans. 1813.) The tenacity of different metals is determined by ascertaining the weight required to break wires of them having the same diameter. Iron appears to possess that property in the greatest, and lead in the least degree. It has been observed by M. Baudrimont that the tenacity of wires of iron, copper, and brass, is much injured by annealing them, (Annal. de Chim. et de Phys. lx. 78.) A few of the malleable metals can be *welded*, or portions of them joined into one by hammering them together. Pieces of iron or platinum may be united in this manner at a bright red heat, and fragments of potassium may be made to adhere by pressing them together with the hand at the temperature of the air. Many metals are only malleable in a low degree, and some are actually brittle,—such as bismuth, antimony, and arsenic.

The metals, with the exception of mercury, are all solid at the temperature of the air, but they may be liquefied by heat. Their points of fusion are very different, as will appear from the following table:

Table of the Fusibility of different Metals.

		FAHR.	DIFFERENT CHEMISTS.
Fusible below a red heat.	Mercury	—39°	
	Potassium	136	Gay-Lussac and Thénard.
	Sodium	190	
	Tin	442	Crichton.
	Bismuth	497	
	Lead	612	
	Tellurium — rather less fusible than lead		Klaproth.
	Arsenic — undetermined.		
	Zinc	773	Daniell.
	Antimony — a little below a red heat.		
	Cadmium	442	Stromeyer.
Infusible below a red heat.	Silver	1873°	Daniell.
	Copper	1996	
	Gold	2016	
	Cobalt — rather less fusible than iron.		
	Iron, cast	2786	Daniell.
	Iron, malleable	Requiring the highest heat of a smith's forge.	
	Manganese		
	Nickel — nearly the same as cobalt.		
	Palladium.		
	Molybdenum	Almost infusible, and not to be procured in buttons by the heat of a smith's forge.	Fusible before the oxi-hydrogen blow-pipe.
	Uranium		
	Tungsten		
	Chromium	Infusible in the heat of a smith's forge, but fusible before the oxi-hydrogen blow-pipe.	
	Titanium		
	Cerium		
	Osmium		
	Iridium		
	Rhodium		
	Platinum		
	Columbium		

The metallic elements are, in general, highly fixed substances, although it is probable that all of them may be dissipated at the highest temperatures. The following metals are so volatile as to be occasionally distilled,—cadmium, mercury, arsenic, tellurium, sodium, potassium, and zinc.

All the metals are capable of uniting with oxygen, but they differ greatly from each other in their affinity for that element. The greater number of them absorb oxygen from dry air at the usual temperature, and undergo oxidation, which is only slight and superficial in many, when they are in mass, but may be complete and perfect in the same metals, when they are highly divided, and in a favourable state for combination, as in the lead and iron pyrophorus exposed to air. The same metals exhibit, at a high temperature, a more intense affinity for oxygen, and combine with the phenomena of combustion.

The metals have been arranged in six groups or sections, differing in their degrees of oxidability: 1. Metals which decompose water even at 32°, with lively effervescence—namely, potassium, sodium, lithium, barium, strontium, calcium. 2. Metals which do not decompose water at 32°, like the metals of the preceding class; they do not decompose it with a lively effervescence, except at a temperature approaching 212°, or even higher, but always much below a red heat. In this class are found magnesium, glucinum, aluminum, zirconium, thorium, yttrium, cerium, and manganese. 3. Metals which do not decompose water except at a red heat, or at the ordinary temperature with the presence of strong acids. This section comprehends iron, nickel, cobalt, zinc, cadmium, tin, chromium, and probably vanadium. Iron is rapidly corroded in water containing carbonic acid, with the evolution of hydrogen. 4. Metals which decompose the vapour of water at a red heat with considerable energy, but which do not decompose water in presence of the strong acids. They are tungsten, molybdenum, osmium, tantalum, titanium, antimony, and uranium. These metals appear to be incapable of decomposing water in contact with acids, because their oxides have but a small basic power, being, indeed, bodies which are ranked among the acids. 5. Metals of which the oxides are not decomposed by heat alone, and which decompose water only in a feeble manner and at a very high temperature. They are also distinguished from the preceding class by their tendency to form basic and not acid oxides. These metals are copper, lead, and bismuth. 6. Metals of which the oxides are reducible by heat alone at a temperature more or less elevated: these metals do not decompose water in any circumstances. They are mercury, silver, palladium, platinum, gold, and probably rhodium and iridium. (Régnault, Annal. de Chim. et de Phys. lxii. 368.) It is to be remarked of nearly all the metals which decompose the vapour of water, and consequently separate hydrogen from oxygen at a certain temperature, that their oxides are reduced, notwithstanding, with great facility by hydrogen gas, and within the same limits of temperature. This anomalous result has already been adverted to in regard to iron (page 181).

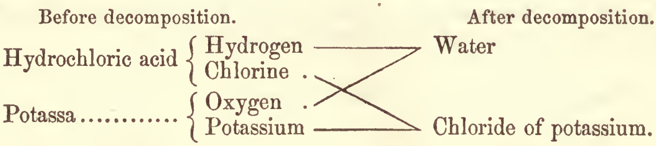
Of the non-metallic elements, hydrogen only forms an oxide capable of uniting as a base with acids. It is a general character of the metals, on the contrary, to form such oxides, if tellurium be excepted, which is more analogous in its chemical properties to sulphur than to the metals. Hence, as the former class are principally salt-radicals, the latter are principally basyls.

The protoxides of metals are uniformly and strongly basic, but this feature becomes less distinct in their superior oxides, and passes into the acid character in the high degrees of oxidation of which some metals are susceptible. Thus, of manganese, the protoxide is a strong base; the sesquioxide basic, but in a less degree than the protoxide; the binoxide indifferent; and the still higher oxides are the manganic and permanganic acids, which are respectively isomorphous with sulphuric and perchloric acids. A few metals which have no protoxides, such as arsenic and antimony, are most remarkable for the acids they form with oxygen, and thus more resemble in their chemical history the elements of the non-metallic class. It is, indeed, impossible to draw an exact line of demarcation between the two classes of elements, either with reference to their physical or chemical properties.

Besides combining with oxygen, metals combine with sulphur, chlorine, and with other salt-radicals, whether simple or compound; and hence sulphides, chlorides, and numerous other series of metallic compounds. Of these series the sulphides most resemble the corresponding oxides of the same metals; the chlorides and other series partake more strongly of the saline character. Each metal, or class of metals, effects combination with oxygen in certain proportions, and combines also with sulphur, chlorine, &c. in the same proportions. Hence, given the formulæ of the oxides of a metal, the formulæ of its sulphides, chlorides, &c. may generally be predicated, as they correspond with the former. Thus the oxides of iron being FeO and Fe_2O_3, the sulphides are FeS and Fe_2S_3, and the chlorides $FeCl$ and Fe_2Cl_3; the oxides of arsenic, or arsenious and arsenic acids, being AsO_3 and AsO_5, the sulphides of that metal are AsS_3 and AsS_5, and the chlorides $AsCl_3$ and $AsCl_5$. But sometimes a metal unites with sulphur in more ratios than with oxygen; both iron and arsenic, for example, possessing each a sulphide to which they have no corresponding oxide, namely, iron pyrites and realgar, of which the formulæ are FeS_2 and AsS_2. The potassium family of metals combine also with three and five equivalents of sulphur, without all uniting with oxygen in such high proportions. Again, certain metals of the magnesian and its allied families, such as manganese and chromium, form acid compounds with oxygen, to which no corresponding sulphides exist, such as manganic and chromic acids, MnO_3 and CrO_3. But the circumstance that these acids are isomorphous with sulphuric acid, and the metals they contain isomorphous with sulphur, appears to be a sufficient reason why there should not be similar sulphur acids. The chlorides of a metal generally correspond in number, as they always do in composition, with the oxides; in some cases they are less numerous, but never, I believe, more numerous than the oxides of the same metal.

Combination takes place within a series; that is, oxides combine with oxides, sulphides with sulphides. Those members of the same series which differ greatly in chemical characters being most disposed to combine together, — as oxygen acids with oxygen bases, sulphur acids with sulphur bases. Chlorides also combine with chlorides, to form double chlorides, and iodides with iodides.

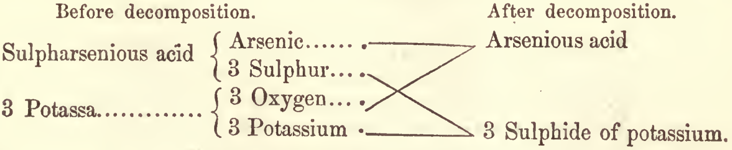
Compounds belonging to different series, on the contrary, do not in general combine together, but often mutually decompose each other when brought into contact. Thus hydrochloric acid and potassa do not unite, one belonging to the chlorine and the other to the oxygen series, but form water and chloride of potassium, by mutual decomposition, as explained in the following diagram: —



In the same manner, sesqui-oxide of iron, when dissolved in hydrochloric acid, produces water and a perchloride of iron corresponding with the peroxide: —

$$3HCl \text{ and } Fe_2O_3 = 3HO \text{ and } Fe_2Cl_3.$$

And in all cases when a metallic oxide dissolves in hydrochloric acid, without evolution of chlorine, the chloride produced necessarily corresponds with the oxide dissolved. Again, orpiment, or sulph-arsenious acid, does not combine with potassa, when dissolved in that alkaline oxide, the first being a sulphur and the second an oxygen compound, but gives rise to the formation of certain proportions of arsenious acid and sulphide of potassium: —



Two pairs of compounds of different series, then, co-exist in the liquid, — an oxygen acid, arsenious acid, which unites with the oxygen base, potassa, and a sulphur base, sulphide of potassium, which unites with undecomposed sulpharsenious acid. Hence the result of dissolving orpiment in potassa is the decomposition of both compounds and formation of two salts of different series, arsenite of potassa and sulpharsenite of sulphide of potassium.

The union of metallic compounds of the oxygen and sulphur series is a rare occurrence. But the red ore of antimony is such a combination, and oxisulphides of mercury also exist. Compounds of metallic oxides with metallic chlorides, and with other highly saline binary compounds, are more frequent; but they are not to be placed in the same category with the compounds of individuals both belonging to the same series, which last are neutral salts. For a metallic oxichloride may generally, if not always, be viewed as a chloride to which a certain proportion of metallic oxide is attached, like constitutional water in a hydrated salt. That metallic oxide is likewise always of the magnesian class, or of a class allied to it. Oxichlorides are then to be associated with those salts of oxygen-acids usually denominated subsalts (page 162); the oxichlorides of lead and of copper,—

$$\mathrm{PbCl + 3PbO} \text{ and } \mathrm{CuCl + CuO},$$

with the subacetates and subsulphates of the same metals.

Arrangement of metallic elements. — A distribution of the metals into three classes is generally made, composed respectively of the metals of the alkalies and alkaline earths, the metals of the earths, and the metals proper. The latter class again is subdivided, according to the affinity of the metals contained in it for oxygen, into two groups — the noble and common metals; the oxides of the former, such as gold, silver, &c., abandoning their oxygen at a high temperature, while the oxides of the latter, lead, copper, &c., are undecomposable by heat alone. In treating of the metals, I shall introduce them in the order which appears to facilitate most the study of their combinations, with a general reference to this classification. For subdivisions, I shall avail myself of the natural families into which the elements have been arranged (page 144), which have the advantage of bringing together those metals of which the compounds are most frequently isomorphous. The different metals will therefore be grouped under the following orders: —

I. Metallic bases of the alkalies — three metals: —

	Oxides.
Potassium	Potassa
Sodium	Soda
Lithium	Lithia

II. Metallic bases of the alkaline earths — four metals: —

	Oxides.
Barium	Baryta
Strontium	Strontia
Calcium	Lime
Magnesium	Magnesia

III. Metallic bases of the earths proper — seven metals: —

	Oxides.
Aluminum	Alumina
Glucinum	Glucina
Zirconium	Zirconia
Yttrium	Yttria
Terbium	Terbia
Erbium	Erbia
Thorium	Thorina

IV. Metals proper, of which the protoxides are isomorphous with magnesia — eight metals: —

Manganese
Iron
Cobalt
Nickel
Zinc
Cadmium
Copper
Lead

V. Other metals proper having isomorphous relations with the magnesian family — seven metals: —

Tin
Titanium
Chromium
Vanadium
Tungsten
Molybdenum
Tellurium

VI. Metals isomorphous with phosphorus — three metals: —

Arsenic
Antimony
Bismuth

VII. Metals proper, not included in the foregoing classes, of which the oxides are not reduced by heat alone — eight metals: —

Uranium.
Cerium.
Lantanum.
Didymium.
Titanium.
Tantalum or Columbium.
Pelopium.
Niobum.

VIII. Metals proper, of which the oxides are reduced to the metallic state by heat (noble metals)—three metals:—

Mercury.
Silver.
Gold.

IX. Metals found in native platinum (noble metals) — six metals:—

Platinum.
Palladium.
Iridium.
Osmium.
Rhodium.
Ruthenium.

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

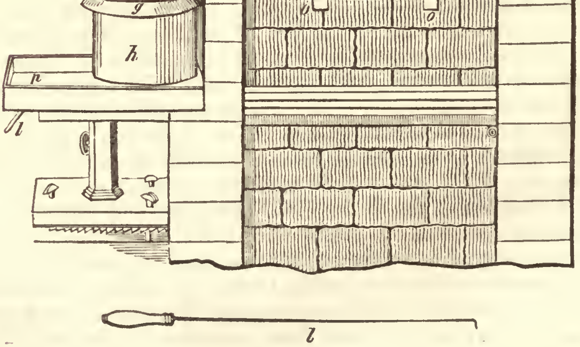
Syn. Kalium. *Eq.* 39 *or* 487.5; K.

The alkalies and earths have long been named and distinguished from each other, but they were not known to be the oxides of peculiar metals till a recent period. The terms applied to the new metallic bases are formed from the names of their oxides, as potassium from potash, and calcium from calx, a name sometimes given to lime; while the original names of the oxides are still retained, as those of ordinary objects, and not superseded by appellations indicating their relation to the metals, such as oxide of potassium for potassa, or oxide of calcium for lime.

Preparation. — In 1807, Sir H. Davy made the memorable discovery that potassa is resolved by a powerful voltaic battery into potassium and oxygen. He placed a moistened fragment of hydrate of potassa on mercury, introducing the terminal wire from the zinc extremity of an active battery (the chloroid) into the fluid metal, and touching the potassa with the other terminal wire (the zincoid); bubbles of oxygen gas appeared at the latter wire, and potassium was liberated at the former, and dissolving in the mercury, was protected from oxidation by the air. To effect this decomposition, Davy employed a battery of 200 pairs of four-inch plates; but an amalgam of potassium may be as readily obtained by a more simple voltaic apparatus, in the manner described at page 221. These processes, however, afford potassium only in minute quantity. Soon after the existence of this metal was known, Gay-Lussac and Thénard discovered that potassa is decomposed by iron at a white heat, and they contrived a process by which a more abundant supply of the metal was obtained. It was afterwards noticed by Curaudau, that potassa, like the oxides of common metals, is decomposed by charcoal as well as by iron, which is the basis of the process for potassium now always followed.

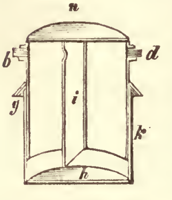
This interesting process is described by Mitscherlich, as it is successfully pursued in Germany. Whenever charcoal is used to deprive a metallic oxide of its oxygen, the former must be in a state of minute division, and be intimately mixed with the latter. Carbonate of potassa requires this precaution the more, that it fuses at a red heat, and is thus apt to separate from the charcoal, and sink below it. It is found that the best means to obtain a proper mixture of these substances is to calcine a salt of potassa containing a vegetable acid, which leaves a large quantity of charcoal when decomposed. Crude tartar (bitartrate of potassa) is preferred, and for one operation six pounds of that salt are ignited in a large crucible or melting-pot provided with a lid, so long as combustible gases are disengaged. The crucible is then withdrawn from the fire, and is found to contain a black mass, which is the mixture of charcoal and carbonate of potassa, known as black flux. It is reduced to powder, while still warm, and immediately mixed with about ten ounces of wood-charcoal in small pieces, or in a coarse powder, from which the dust has been separated by a sieve. The use of this additional charcoal is to act as a sponge, and absorb the potassa when liquefied by heat. The mixture is introduced into a bottle of wrought iron, and a mercury bottle (page 224) answers well for the purpose, but must be heated to redness beforehand, to expel a little mercury that remains in it. The mouth of the bottle is enlarged a little by means of a round file, and a straight iron tube of 4 or 5 inches in length fitted into the opening, by grinding. The bottle and tube thus form a retort, which is supported horizontally in a brick furnace, as represented (fig. 165) in which *a* is the iron bottle resting upon two bars of iron *o o*, to which it may also be firmly bound by iron wire. These bars cross the furnace at

FIG. 165.



a height of 5 or 6 inches above the grate-bars. A mixture of equal parts of coal and coke makes an excellent fuel for this furnace. The tube *b* of the bottle projects through an aperture in the side-wall of the furnace, and enters a receiver of a peculiar construction required to condense the potassium, which distils over. This receiver is composed of two separate copper cylinders or oval boxes, hard soldered, similar in form and size, which are represented in section (fig. 166), the one, *b n d*, being introduced within the other, *g h k*, and thus forming together a vessel of which *b n d* is the cover. It will also be observed that *b d* is divided into two cells by a diaphragm, *i*, of the same length as the cylinder, and descending with it to within two inches of the bottom, *h*, of *g h k*. A ribbon of copper, *g*, is soldered around *b n d*, so as to form a ledge, which is seen in both figures, and serves as a support for a cage of iron-wire, *c d*, placed over the receiver during the distillation, to hold ice, and also to shed the water from the liquefaction of that ice, which falls into a tray, *p*, below, and flows off by the tube, *l*. The cover has also two short copper tubes, *d* and *b*, of which the copper of *b* is notched so as to clasp firmly by its elasticity the tube *b* from the iron bottle, which is fitted into it. The other tube, *d*, which is exactly opposite to *b*, is fitted with a cork, and the diaphragm, *i*, has a small hole in it to allow of a rod being passed through *b* and *d*. In the same part of the apparatus is a third opening, to which a glass tube, *x*, is fitted by a cork, for the escape of uncondensible gases. The receiver is filled to about one-third with rectified petroleum, a liquid containing no oxygen, so as to come nearly to, but not to cover, the bottom of the partition, *i*. The length of the bottle is 11 inches, its width 4, and the other parts of the apparatus are designed upon the same scale.

Fig. 166.



Potassium and carbonic oxide gas are the principal products of the decomposition of the carbonate of potassa, but other substances besides these are found in the receiver; namely, a black mass very rich in potassium, some oxalate and croconate of potassa and free potassa, with a portion of charcoal powder carried over mechanically. Part of these products appears to be formed, after the reduction of the potassium, by the mutual reaction of that metal, carbonic oxide and petroleum. The process is found to succeed best when the iron tube, *b*, is so short that it can be maintained at a red heat through its whole length during the operation, while the receiver is kept at a very low temperature; the potassium then falls from the tube, drop by drop, into the receiver, and does not remain long in contact with carbonic oxide, which is known to combine readily with that metal. One or two other points should always be attended to. The connexion between the tube *b* and the receiver is not made till the iron bottle has been heated to redness, to allow of the escape of a little water, and of a trace of mercury, which had remained in the bottle in the state of vapour, and which come off first. The joining of the tube *b* is not air-tight at first, and allows a little potassium vapour to escape, but this burns and forms potassa, which immediately closes the openings. This tube being always incandescent and the refrigeration properly made, the reduction sometimes proceeds without interruption. But the tube is sometimes obstructed, as appears by the gases ceasing to escape by *x*. Haste must then be made to open the tube *b*, and to clear it by means of a flattened iron rod, *l*, slightly hooked at its anterior extremity. Care has been taken to mark on this rod, with the scratch of a file, how far it has to penetrate into the apparatus to reach the mouth of the bottle, and it must not be introduced farther. The current of air through the furnace is regulated by a register valve in the chimney, and the fire stirred frequently so as to prevent the formation of cavities; the operator being guided in the management of the fire by the rapidity of the current of gas which escapes by the tube *x*. To terminate the operation, the grate bars may be thrown down, by which the fuel will fall into the ash-pit. The quantity of crude tartar mentioned yields about 4 ounces of potassium, which is about 4 per cent. of its weight. The potassium thus obtained, containing a little carbon chemically combined with it, is submitted, together with the black mass found in the receiver, to a second distillation. For this purpose a smaller iron bottle with a bent tube may be employed, the end of which is covered by rectified petroleum in a capacious flask, used as a receiver. (Mitscherlich, Elémens de Chimie, iii. 8). [*See Supplement*, p. 805.]

Properties.—Potassium is solid at the usual temperature, but so soft as to yield like wax to the pressure of the fingers. A fresh surface has a white colour, with a shade of blue, like steel, but is almost instantly covered by a dull film of oxide when exposed to air. The metal is brittle at 32°, and has been observed crystallized in cubes: it is semi-fluid at 70°, and becomes completely liquid at 150°. It may be distilled at a low red heat, and forms a vapour of a green colour. Potassium is considerably lighter than water, its density being 0.865 at 60°.

Potassium oxidates gradually without combustion when exposed to air; but heated till it begins to vaporize, it takes fire and burns with a violet flame. The avidity of this metal for oxygen is strikingly exhibited when a fragment of it is thrown upon water. It instantly decomposes the water, and so much heat is evolved as to kindle the potassium, which moves about upon the surface of the water, burning with a strong flame, of which the vivacity is increased by the combustion of the hydrogen gas disengaged at the same time. A globule of fused potassa remains, which continues to swim about upon the surface of the water for a few seconds, but finally produces an explosive burst of steam, when its temperature falls to a certain point, illustrating the phenomenon of a drop of water on a hot metallic plate (page 64.)

Potassium appears to have the greatest affinity of all bodies for oxygen at temperatures which are not exceedingly elevated. It decomposes nitrous and nitric oxides, and also carbonic oxide gas at a red heat, although potassa is reduced to the metallic state by charcoal at a white heat. It has already been stated that the oxides and fluorides of boron and silicon are decomposed by potassium, and besides these elements, several of the metallic bases of the earths are obtained by means of this metal. It is, indeed, a reducing agent of the greatest value.

COMPOUNDS OF POTASSIUM.

Potassa, or potash; KO; 590 *or* 47.26.—Potassium exposed in thin slices to dry air becomes a white matter, which is the protoxide of potassium or potassa. This compound is fusible at a red heat, and rises in vapour at a strong white heat. It unites with water, with ignition, and forms a fusible hydrate, which is the ordinary condition of caustic potassa.

The hydrate of potassa is obtained in quantity from the carbonate of potassa. Equal weights of that salt and of quicklime are taken, the latter of which is slaked with water, and falls into a powder consisting of hydrate of lime; the former is dissolved in from 6 to 10 times its weight of water, and both boiled together for half an hour in a clean iron pan. The lime abstracts carbonic acid from the potassa and becomes carbonate of lime; a reaction which may be illustrated by adding lime-water to a solution of carbonate of potassa, when a precipitate of carbonate of lime falls. When the potassa has been deprived entirely of carbonic acid, a little of the clear liquid taken from the pan will be found not to effervesce upon the addition of an acid to it. It is remarkable that the decomposition is never complete if the carbonate of potassa be dissolved in less than the prescribed quantity of water. Liebig has observed that a concentrated solution of potassa decomposes carbonate of lime, and consequently hydrate of lime could not, in the same circumstances, decompose carbonate of potassa. The pan, being covered by a lid, may be allowed to cool; when the insoluble carbonate of lime and the excess of hydrate of lime subside, a considerable quantity of the clear solution of potassa may be drawn off by a syphon, and the remainder may be obtained clear by filtration. In the latter operation a large glass funnel may be employed, to support a filter of washed cotton calico, into which what remains in the pan is transferred. A small portion of liquid, which passes through turbid at first, should be returned to the filter. As the solution of potassa absorbs carbonic acid, it is proper to conduct its filtration with as little exposure to air as possible; on which account the mouth of the the funnel should be covered by a plate, and the liquid which flows from it be immediately received in a bottle, in the mouth of which the funnel may be supported. The bottle in which potassa is preserved should not be of crystal, or of a material containing lead, as the alkali corrodes such glass, particularly when its natural surface has been cut.

To obtain the solid hydrate of potassa, the preceding solution is rapidly evaporated in a clean iron pan or silver basin, till an oily liquid remains at a high temperature, which contains no more than a single equivalent of water. This liquid is poured into cylindrical iron moulds to obtain it in the form of sticks, which are used by surgeons as a cautery, and are the *potassa* or *potassa fusa* of the Pharmacopœia; a form in which it is also convenient to have potassa for some chemical purposes. The sticks generally contain a portion of carbonate of potassa, besides a little oxide of iron and peroxide of potassium, the last of which gives occasion to the evolution of a little oxygen gas when the sticks are dissolved in water. To obtain hydrate of potassa free from carbonate, the sticks are dissolved in alcohol, in which the foreign impurities are insoluble, and the alcoholic solution is evaporated to dryness.

The pure and fused hydrate of potassa is a solid white mass of a structure somewhat crystalline, of sp. gr. 1.706, fusible at a heat under redness. It is a protohydrate, and cannot be deprived of its combined water by the most intense heat. It destroys animal textures. It rapidly deliquesces in damp air, from the absorption of moisture: is soluble in half its weight of water, and also in alcohol. Mixed in powder with a small quantity of water, it forms a second crystalline combination, which is a terhydrate; and its solution in water affords, at a very low temperature, crystals in the forms of four-sided tables and octohedrons, which are a pentahydrate, $KO.HO+4HO$. [*See Supplement*, p. 806.]

The solution of potassa, or potassa ley, has a slight but peculiar odour, characteristic of caustic alkalies, which they acquire from their action upon organic matter, derived from the atmosphere or other sources. The skin and other animal substances are dissolved by this liquid. It is highly caustic, and its taste intensely acrid. It has those properties which are termed alkaline, in an eminent degree. It neutralizes the most powerful acids, restores the blue colour of reddened litmus, changes the blue infusion of cabbage into green, but in a short time altogether destroys these vegetable colours. It acts upon fixed oils, and converts them into soaps, which are soluble in water. It absorbs carbonic acid with great avidity from the air, on which account it should be preserved in well-stopped bottles.

The presence of free potassa or soda, in solutions of their carbonates, may be discovered by nitrate of silver, the oxide of which is precipitated of a brown colour by the caustic alkali, while the white carbonate of silver only is precipitated by the pure carbonated alkali. Potassa, whether free or in combination with an acid as a soluble salt, may be discovered and distinguished from soda and other substances, by means of certain acids, &c., which form sparingly soluble compounds with that alkali. A strong solution of tartaric acid produces a precipitate of bitartrate of potassa, in a liquid containing 1 per cent. of any potassa salt. The precipitate is crystalline, and does not appear immediately, but is thrown down on stirring the liquid strongly, and soonest upon the lines which have been described on the glass by the stirrer. A similar precipitation is occasioned in salts of potassa by perchloric acid. Also by bichloride of platinum, which forms the double chloride of platinum and potassium, in granular octohedrons of a pale yellow colour. In the separation of potassa for its quantitative estimation, the last reagent is preferred, and is added in excess to the potassa solution, together with a few drops of hydrochloric acid, which is then evaporated by a steam heat to dryness. The dry residue is washed with alcohol, which dissolves up everything except the double chloride of platinum and potassium. Ammonia, also, is thrown down by bichloride of platinum; but when the chloride of platinum and ammonium is heated to redness, nothing is left except spongy platinum, while the chloride of platinum and potassium leaves all its potassium in the state of chloride mixed with the platinum. Potassa is likewise separated from acids by means of fluosilicic acid, which throws down a light gelatinous precipitate, the double fluoride of silicon and potassium. Carbazotic acid also produces a yellow crystalline precipitate in solution of potassa.

Salts of potassa, more particularly the chloride, nitrate, and carbonate, communicate to flame a pale violet tint.

Potassa is the base which in general exhibits the highest affinity for acids; it precipitates lime and the insoluble metallic oxides from their solutions in acids. This alkali is employed indifferently with soda for a variety of useful purposes. The principal combinations of potassa with acids will be described after the binary compounds of potassium.

Peroxide of potassium, KO_3. — Heated strongly in air or oxygen, potassium combines with three equivalents of oxygen. The ultimate residue on calcining nitrate of potassa at red heat has been said to be the same compound, but Mitscherlich finds that residue to be potassa. The peroxide of potassium is decomposed by water, being converted into hydrate of potassa, with evolution of oxygen gas.

When potassium is burned with an imperfect supply of air, a grey matter is formed, which Berzelius believed to be a suboxide of potassium. It is not more stable than the peroxide.

Sulphides of potassium. — Sulphur and potassium, when heated together, unite with incandescence, and in several proportions, two of which correspond respectively with the protoxide and peroxide of potassium. The *protosulphide* may be obtained by transmitting hydrogen gas over sulphate of potassa, heated in a bulb of hard glass to full redness, when the whole oxygen of the salt is carried off as water, and the sulphur remains in combination with potassium, forming a fusible compound of a light brown colour. Sulphate of potassa calcined with one-fourth of its weight of pounded charcoal or pit-coal, in a covered Cornish crucible, at a bright red heat, is converted into a black crystalline mass, which is also protosulphide of potassium, with generally a small quantity of a higher sulphide, arising from the combination of the silica of the crucible with potassa of the sulphate. If lamp-black be used instead of charcoal, the sulphide of potassium formed having a great affinity for oxygen, and being in a highly divided state, takes fire when exposed to the air, and forms a pyrophorus. The solution of the protosulphide in water is highly caustic; it is decomposed by acids with effervescence, from the escape of hydrosulphuric acid, but without any deposit of sulphur. Being a sulphur base, it combines without decomposition with sulphur acids.

This sulphide unites directly with hydrosulphuric acid, forming $KS.HS$; and the compound may be otherwise formed, namely, by transmitting a stream of hydrosulphuric acid through caustic potassa, so long as the gas is absorbed. It is often named the *bihydrosulphate of potassa.* It is analogous in composition to hydrate of potassa ($KO.HO$) in the oxygen series.

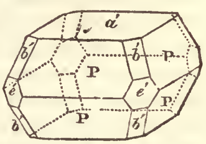
The *trisulphide* is formed when anhydrous carbonate of potassa, mixed with half its weight of sulphur, is maintained at a low red heat so long as carbonic acid gas comes off. Of four proportions of potassa, three become sulphide of potassium, while sulphuric acid is formed, which neutralizes the fourth proportion of potassa: $4KO$ and $10S = 3KS_3$ and $KO.SO_3$. With carbonate of potassa and sulphur, in equal weights a similar action occurs, at a temperature above the fusing point of sulphur, but five, instead of three, proportions of sulphur then unite with one of potassium, and a *pentasulphide* is formed. With a larger proportion of carbonate of potassa the same sulphide is also produced, provided the temperature does not much exceed the boiling point of sulphur, and the excess of carbonate fuses along with it, without undergoing decomposition. A sulphide obtained by fusing sulphur and carbonate of potassa together has a liver-brown colour, and hence its old pharmaceutic name *hepar sulphuris.* The three sulphides described are deliquescent, and are all soluble in water, the higher sulphides giving red solutions. They may, indeed, be prepared by heating sulphur, in proper proportions, with caustic potassa. A simultaneous formation of hyposulphurous acid then occurs, as already explained (page 304). The preparation, *precipitated sulphur*, is obtained by adding an excess of hydrochloric acid to these solutions, when much sulphur is thrown down, although the potassium be only in the state of protosulphide, for the hydrosulphuric acid, arising from the action of the acid on that sulphide, meets hyposulphurous evolved at the same time from the decomposition of the hyposulphite, with the formation of water and sulphur. The excess of sulphur in the alkaline sulphide also precipitates at the same time. The peculiar whiteness of precipitated sulphur is owing, according to Rose, to its containing a little bisulphide of hydrogen.

Chloride of potassium; eq. 74.5 *or* 931.25; KCl. — Formed by the combustion of potassium in chlorine, or by neutralizing hydrochloric acid by potassa or its carbonate. It is also derived in considerable quantity from kelp (page 352). It crystallizes in cubes and rectangular prisms, resembles common salt in taste, and is considerably more soluble in hot than in cold water. According to the observations of Gay-Lussac, 100 parts of water dissolve of this salt 29.21 parts at 0° C.; 34.53 parts at 19°.35; 43.59 parts at 52°.39; 50.93 parts at 79°.58, and 59.26 parts at 109°.6 C. When pulverised and dissolved in four times its weight of cold water, it produces a depression of temperature of 20½ degrees; while chloride of sodium, dissolved in the same manner, lowers the temperature only 3.4 degrees. Upon the difference between two salts in this property, M. Gay-Lussac founded a method of estimating their proportions in a mixture. Chloride of potassium is principally consumed in the manufacture of alum. Rose observed that chloride of potassium unites with anhydrous sulphuric acid, $KCl+2SO_3$. The same salt unites with terchloride of iodine, $KCl.ICl_3$.

Iodide of potassium; eq. 165.36 *or* 2067; KI. — This salt is obtained by dissolving iodine in solution of potassa till neutral, evaporating to dryness, and heating to redness, to decompose the portion of iodate of potassa formed. M. Freundt recommends to add a little charcoal to the mixed iodide and iodate. Iodide of potassium is more soluble in water than the chloride, and may be obtained in cubes or rectangular prisms, which are generally white and opaque, and have an alkaline reaction from the presence of a trace of carbonate of potassa. Iodide of potassium is also dissolved by alcohol, but in a much less proportion than by water. The dry salt does not combine with more iodine, but in conjunction with a small quantity of water (I believe 4 equivalents) it absorbs the vapour of iodine with great avidity, and runs into a liquid of a deep red, almost black, colour. According to Baup, a saturated solution of iodide of potassium may dissolve so much as two equivalents of iodine, but allows one equivalent to precipitate when diluted. Iodide of potassium, which is often called the *hydriodate of potassa*, is much used in medicine; it is not poisonous even in doses of several drachms. Its solution is also employed as a vehicle for iodine itself, 20 grains of iodine and 30 grains of iodide of potassium being usually dissolved together in 1 ounce of water. The bromide of potassium is capable also of dissolving bromine, but the solution of chloride of potassium has no affinity for chlorine.

Ferrocyanide of potassium. Yellow prussiate of potassa; $K_2.FeCy_3+3HO$; *eq.* 184+27 *or* 2300+337.5. — This important salt is formed when carbonate of potassa is fused at a red heat in an iron pot, with animal matter, such as dried blood, hoofs, clippings of hides, &c., and is the product of a reaction to be hereafter described. This salt occurs in a state of great purity in commerce. It is of a lemon yellow colour, and crystallized in large quadrangular tables, with truncated angles and edges, belonging to the square prismatic system. The crystals contain 3 equivalents of water, which they lose at 212°, are soluble in 4 parts of cold and 2 parts of boiling water, and are insoluble in alcohol. The taste of this salt is saline, and it is not

FIG. 167.



poisonous. By a red heat it is converted, with escape of nitrogen gas, into carburet of iron and cyanide of potassium; but with exposure to air the latter salt absorbs oxygen, and becomes cyanate of potassa. This salt is represented by Liebig as containing a salt-radical, ***Ferrocyanogen***, composed of 1 eq. of iron and 3 eq. of cyanogen, or $FeCy_3$. This salt-radical is bibasic, and is in combination with 2 eq. potassium in the salt, as will be seen by reference to its formula. The same salt has been represented by myself as a compound of a tribasic salt-radical *prussine* (3Cy), with Fe+2K. But its reactions with other salts are most easily stated on the former view of its constitution. The iron in this salt is not precipitated by alkalies. When ferrocyanide of potassium is added to salts of lead and various other metallic solutions, it produces precipitates, in which two equivalents of the lead or other metal are substituted, in combination with ferrocyanogen, for the two equivalents of potassium. In salts of sesquioxide of iron, ferrocyanide of potassium produces the well-known precipitate, Prussian blue.

Ferricyanide of potassium, Red prussiate of potassa; $3K.Fe_2Cy_6$; *eq.* 329 *or* 4112.5. — This salt, which, like the last, is a valuable reagent, is formed by transmitting chlorine gas through a solution of the ferrocyanide of potassium, till it ceases to give a precipitate of Prussian blue with a persalt of iron, and no longer. One-fourth of the potassium of the ferrocyanide is converted into chloride, from which the resulting ferricyanide may be separated by crystallization. It forms right rhombic prisms, which are transparent and of a fine red colour. The crystals are anhydrous, soluble in 3.8 parts of cold, and in less hot water. They burn with brilliant scintillations when held in the flame of a candle. The solution of this salt is a delicate test of iron in the state of protoxide, throwing down from its salts a variety of Prussian blue, in which the 3K of the formula are replaced by 3Fe. Liebig views the red prussiate of potassa as containing a salt-radical, *Ferricyanogen*, or ferridcyanogen, Fe_2Cy_6, differing from ferrocyanogen in having twice its atomic weight and in being tribasic.

Cyanide of potassium; eq. 65 *or* 812.5; KCy. — The preparation of this salt is attended with difficulty, owing to the action of the carbonic acid of the air upon its solution, which evolves hydrocyanic acid, and the tendency of the solution itself to undergo spontaneous decomposition, even in close vessels. It may be formed by adding absolute hydrocyanic acid, or a strong solution of that acid, to a solution of potassa in alcohol; a portion of the cyanide falls down as a white crystalline precipitate, which should be washed with alcohol and dried, and an additional quantity is obtained by evaporating the liquid in a retort. But it is prepared with more advantage from the ferrocyanide of potassium, already described. That salt is carefully dried and reduced to a fine powder, 8 parts of which are mixed with 3 parts of carbonate of potassa and 1 part of charcoal, and exposed to a strong red heat in a closed iron crucible, or other convenient vessel. The mass is reduced to powder, placed in a funnel, moistened with a little alcohol, and then washed with cold water. The strong solution of cyanide of potassium which comes through is colourless, and must be rapidly evaporated to dryness in a porcelain basin, and fused at a red heat. The crude salt, obtained by ignition without charcoal, contains a little cyanate of potassa, but this does not interfere with its use for forming and dissolving cyanides of gold and silver, for the processes of voltaic gilding and plating.

Cyanide of potassium crystallizes in colourless cubes, which become opaque and deliquesce in damp air, and are very soluble in water. It bears a red heat without decomposition in close vessels, but with exposure to air absorbs oxygen, and becomes cyanate of potassa (KO.CyO). Its solution smells of hydrocyanic acid, being decomposed by carbonic acid. The action of cyanide of potassium upon the animal economy is equally powerful with that of hydrocyanic acid, and as the dry salt may be preserved in a well-stopped bottle without change, it is preferable to the acid, which is far from stable. Red oxide of mercury dissolves freely in the solution of cyanide of potassium, cyanide of mercury being formed and potassa set free. The purity of the alkaline cyanide may be ascertained from this property; 12 grains of the pure cyanide dissolving 20 grains of finely-pulverised oxide of mercury.

Hydrocyanic acid for medical purposes is conveniently prepared from this cyanide. 24 grains of cyanide of potassium, 56 grains of tartaric acid in crystals, and 1 ounce of water, are agitated together in a stout phial closed by a cork. The liquid is afterwards separated by filtration from the precipitate of bitartrate of potassa; it contains 10 grains of hydrocyanic acid, or rather more than 2 per cent. (Dr. Clark).

Sulphocyanide of potassium; $K.CyS_2$; 1222.2 *or* 97.92. — Sulphocyanogen is a salt-radical consisting of 2 eq. sulphur and 1 eq. cyanogen, which is formed on fusing the ferrocyanides with sulphur. To obtain it in combination with potassium, the ferrocyanide of potassium, made anhydrous by heat and reduced to a fine powder, is mixed with an equal weight of flowers of sulphur in a common cast-iron pot (pitch pot), and kept in a state of fusion for half an hour at a temperature above the melting point of sulphur, but below that at which bubbles of gas escape through the melted mass. No cyanogen is evolved or decomposed, and the residuary matter is a mixture of sulphocyanide of potassium and protosulphocyanide of iron, with the excess of sulphur. Both sulphocyanides dissolve in water, and give a solution which is colourless at first, but soon becomes red from oxidation of the sulphocyanide of iron. To get rid of the iron, carbonate of potassa is added to the boiling solution, so long as a precipitate of carbonate of iron falls, and the liquid is afterwards filtered. This solution gives crystals of sulphocyanide of potassium, when evaporated, which may be freed from any adhering carbonate of potassa by dissolving them in alcohol. The salt crystallizes in long white striated prisms, which are anhydrous, and resemble nitrate of potassa in their appearance and taste. They deliquesce in a damp atmosphere, and are very soluble in hot alcohol, from which the salt crystallizes on cooling. The sulphocyanide of potassium communicates a blood-red colour to solutions of salts of sesquioxide of iron, and is consequently employed as a test of that metal in its higher state of oxidation. The red solution is made perfectly colourless by a moderate dilution with water, when the iron is not present in excess. The sulphocyanide of potassium has been detected in the saliva of man and the sheep.

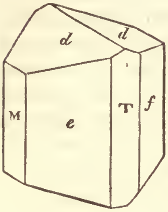
SALTS OF OXIDE OF POTASSIUM.

Carbonate of potassa; $KO.CO_2$; *eq.* 69 *or* 862.5. — This useful salt is principally obtained from the ashes of plants. Potassa is always contained in a state of combination in clay and other minerals which form the earthy part of soil, and appears to be a constituent of soil essential to vegetation. The alkali is appropriated by plants, and is found in their sap combined with vegetable acids, particularly with oxalic and tartaric acids; also with silicic and sulphuric acids, and as chloride of potassium. When the plants are dried and burned, the salts of the vegetable acids are destroyed, and leave carbonate of potassa: shrubs yielding three, and herbs five times as much saline matters as trees; and the branches of trees being more productive than their trunks—a distribution which may depend upon the potassa existing chiefly in the sap. The whole ashes from wood seldom exceed 1 per cent. of its weight, of which 1-6th may be saline matter. The solution, evaporated to dryness, yields *potashes*; and these, partially purified and ignited, form *pearlash*. The carbonate is mixed in the latter with about 20 per cent. of foreign salts, principally sulphate of potassa and chloride of potassium. The carbonate of potassa is obtained, in a state of greater purity, by dissolving pearlash in an equal weight of water, then separating the solution from undissolved salts, and evaporating it to dryness.

Carbonate of potassa is prepared of greater purity for chemical purposes, by igniting bitartrate of potassa; or better, by burning together 2 parts of that salt and 1 of nitre. In the latter process, the carbon and hydrogen of the tartaric acid are destroyed by the oxygen of the nitric acid, and carbonate of potassa remains mixed with charcoal, from which it may be separated by solution and filtration.

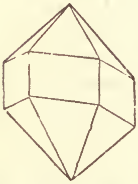
Carbonate of potassa has an acrid, alkaline taste, but is not caustic. It gives a green colour to the blue infusion of cabbage. This salt is highly deliquescent, and soluble in less than an equal weight of water at 60°. It may be crystallized with two equivalents of water. Added to solutions of salts of lime, lead, &c., it throws down insoluble carbonates. It is more frequently used than the caustic alkali, to neutralize acids and to form the salts of potassa.

Fig. 168.



Bicarbonate of potassa; $HO.CO_2 + KO.CO_2$; *eq.* 100 *or* 1250. — Formed by transmitting a stream of carbonic acid gas through a saturated cold solution of the neutral carbonate. It is soluble in four times its weight of water at 60°, and in less water at 212°. The solution has an alkaline taste and reaction, but is not acrid; it does not thrown down magnesia from its soluble salts; it loses carbonic acid when evaporated at all temperatures, and becomes neutral carbonate. The salt contains one proportion of water, which is essential to it, and crystallizes well in prisms of eight sides, having dihedral summits. The existence of a sesquicarbonate of potassa is doubtful.

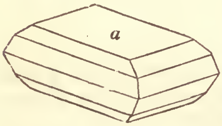
Fig. 169.



Sulphate of potassa; $KO.SO_3$; *eq.* 87 *or* 1087.5. — This salt precipitates when oil of vitriol is added, drop by drop, to a concentrated solution of potassa. It is generally prepared by neutralizing the residue, composed of bisulphate of potassa, of the nitric acid process (page 260), and crystallizes in double pyramids of six faces, or in oblique four-sided prisms. The crystals are anhydrous, unalterable in air, and they decrepitate strongly when heated; their density is 2.400. The sulphate is one of the least soluble of the neutral salts of potassa: 100 parts of water dissolve 8.36 parts of this salt at 32°, and 0.09666 parts more for each degree above that point.

Hydrated bisulphate of potassa, or sulphate of water and potassa; $HO.SO_3 + KO.SO_3$; *eq.* 136 *or* 1700: the fusible salt remaining, when nitrate of potassa is decomposed in a retort by two equivalents of oil of vitriol. Below 386.6° (197° C.), it is a white crystalline mass. This salt is very soluble in water, but is partially decomposed by that liquid, and deposits sulphate of potassa. It crystallizes from a strong solution in rhombohedral crystals, of which the form is identical with one of the forms of sulphur. But this salt is dimorphous, and crystallizes from a state of fusion by heat in large crystals, which have the form of felspar (Mitscherlich). Its density is 2.163. The excess of acid in this salt acts upon metals and alkaline bases very much as if it were free.

Fig. 170.

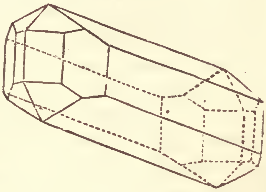


Hydrated sesquisulphate of potassa; $HO.SO_3 + 2(KO.SO_3)$. — A salt in prismatic needles discovered by Mr. Phillips, and which has also accidentally occurred since to Mr. Jacquelin. It is decomposed by water; the circumstances necessary for its formation are unknown.

Sulphate of potassa combines with *hydrated nitric and phosphoric acids,* as well as with hydrated sulphuric acid. On dissolving the neutral salt in nitric acid, a little nitre and hydrated bisulphate of potassa are formed, with a large quantity of a salt in oblique prisms, of which the formula is $HO.NO_5 + 2(KO.SO_3)$. This last salt fuses at 302° (150° C.); its density is 2.38 (Jacquelin). The compound with phosphoric acid is formed by dissolving sulphate of potassa in a syrupy solution of that acid, and crystallizes in oblique prisms of six sides, which fuse at 464° (240° C.), and of which the density is 2.296 (Jacquelin). Its formula is $3HO.PO_5 + 2(KO.SO_3)$. It will be observed that both these compounds agree with Mr. Phillips's sesquisulphate in having 2 eq sulphate of potassa to 1 eq. of hydrated acid. (Annales de Chimie, lxx).

Nitrate of potassa, Nitre, Saltpetre; $KO.NO_5$; *eq.* 101 *or* 1262.5. — Nitric acid is formed in the decomposition of animal matters containing nitrogen, when they are exposed to air, and are in contact with alkaline substances. It appears to be largely produced in this way in the soil of certain districts of India, from which nitrate of potassa is obtained by lixiviation. Nitrous soils always contain much carbonate of lime, the debris of tertiary calcareous rocks, in which the oxygen and nitrogen of the air unite, according to some, assisted by the porous structure of the rock, and under the influence of an alkaline base, so as to generate nitric acid without the intervention of animal matter. But this conjecture is not founded upon experiment; nor is it a necessary hypothesis, since nitrifiable rocks are never entirely destitute of organic matter. Nitrate of potassa is also prepared in some countries of Europe, by imitating the natural process, in artificial nitre beds, wherein nitrate of lime is formed, and afterwards converted into nitrate of potassa by the addition of wood-ashes to the lixivium.[1]

Fig. 171.



Nitrate of potassa generally crystallizes in long striated six-sided prisms, is anhydrous, unalterable in the air, fusible into a limpid liquid by a heat under redness, in which condition it is cast in moulds, and forms *sal prunelle*. Its density is 1.933 (Dr. Watson). According to Gay-Lussac 100 parts of water dissolve 13.3 parts of this salt at 32°, 29 parts at 64.4°, 74.6 parts at 96.8°, and 236 parts at 206.6°. The taste of the solution is cooling and peculiar; it has considerable antiseptic properties. Nitre is insoluble in absolute alcohol.

From the large quantity of oxygen which nitre contains, and the facility with which it imparts that element to combustibles at a red heat, it is much employed in making gunpowder and other deflagrating mixtures. An intimate mixture of nitre in fine powder with one-third of its weight of wood-charcoal, when touched by a body in ignition, burns with great brilliancy, but without explosion. A mixture of 3 parts of nitre, 2 of dry carbonate of potassa, and 1 of sulphur, forms *pulvis fulminans,* which, heated gently till it enters into fusion, inflames suddenly, and explodes with a deafening report. The violence of the explosion is caused by the reaction between the sulphur and nitre being instantaneous, from their fusion and perfect intermixture, and the consequent sudden formation of much nitrogen gas from the decomposition of nitric acid. Gunpowder contains both sulphur and charcoal, of which the former serves the purpose of accelerating the process of deflagration and supplying heat, while the latter supplies much of the gas, to the formation of which the available force of the explosion is due. Gunpowder yields about 300 times its volume of gas, measured when cold; but its explosive force is greater than this indicates, from the high temperature of the gas, and not less than 1000 atmospheres. The ordinary proportions of gunpowder approach very nearly 1 eq. of nitre, 1 of sulphur, and 3 of carbon, as will be seen by the following comparison:—

Composition of Gunpowder.

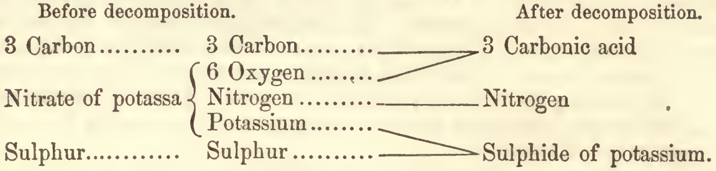
	Theoretical Mixture.	English.	Prussian.
Sulphur	11.9	12.5	11.5
Charcoal	13.5	12.5	13.5
Nitre	74.6	75.	75.
	100.0	100.0	100.0

---

[1] The observations and original experiments upon nitrification, of Professor Kuhlman, are valuable, but do not lead to any general theory of the process. He did not succeed in causing oxygen and nitrogen gases to combine by means of spongy platinum, but he found that under the influence of that substance (1°) all vaporisable compounds of nitrogen, including ammonia, mixed with air, with oxygen, or with an oxidating gas, change into nitric acid or peroxide of nitrogen; and (2°) that all the vaporisable compounds of nitrogen, including nitric acid, mixed with hydrogen or a hydrogenous acid, give rise to ammonia.—(Memoirs of the Academy of Sciences of Lille, 1838, and Liebig's Annalen, xxix. 272, 1839.)

By the combustion of the mixture, carbonic acid and nitrogen gases are formed, with a solid residue of protosulphide of potassium. Thus: —

Deflagration of Gunpowder.



A portion of the potassa is always converted into sulphate of potassa, which must interfere with the exactness of this decomposition. Blasting powder is composed of 20 sulphur, 15 charcoal, and 65 nitre; the proportion of sulphur being increased, by which a more powerfully explosive mixture is obtained, but which is not suitable for fire-arms, as they are injured by an excess of sulphur. The most inflammable charcoal is employed in making gunpowder; which is obtained by calcining branches of about $\frac{3}{4}$ths of an inch in diameter, in an iron retort, for a considerable time, at a heat scarcely amounting to redness, and which has a brown colour without lustre. The granulation of gunpowder increases its explosive force. A charge is thus made sufficiently porous to allow flame to penetrate it, and to kindle every grain composing it at the same time. But still the discharge of gunpowder is not absolutely instantaneous; and it is remarkable that other explosive compounds which burn more rapidly than gunpowder, such as fulminating mercury, are not adapted for the movement of projectiles. Their action in exploding is violent but local; if substituted for gunpowder in charging ordinary fire-arms, they would shatter them to pieces, and not project the ball. It is a common practice to mix with the charge of blasting powder, used in mining, a considerable bulk of sawdust, which renders the combustion of the powder still slower, but productive of a sustained effort, most effectual in moving large masses.

Chlorate of potassa; $KO.ClO_5$; *eq.* 122.5 *or* 1531.25. — This salt is the result of a reaction between chlorine and potassa, which has already been explained (page 341). In the preparation of chlorate of potassa, a strong solution of two or three pounds of carbonate of potassa is made, and chlorine passed through it. The gas is conducted into the liquid by a pretty wide tube, or better by a tube terminated by a funnel, to prevent its being choked by the solid salt which is formed. A stage in the process can be observed before the liquid has discharged much carbonic acid, when bicarbonate, chlorate, and hypochlorite of potassa exist together in solution, and a considerable quantity of chloride of potassium is deposited. The latter salt is removed, and the current of chlorine continued till the liquid, which is often red from hypermanganic acid, becomes colourless or yellow, and ceases to absorb the gas. A considerable quantity of chlorate of potassa is deposited in tubular shining crystals, which are purified by solution and a second crystallization; and more of the same salt is obtained from the liquid evaporated and set aside to crystallize; the separation of the chlorate from chloride of potassium depending upon the solubility at a low temperature of the former salt being greatly less than that of the latter.

The chlorate of potassa may be prepared more economically by exposing to a current of chlorine gas a mixture of 7.6 parts of carbonate of potassa, and 16.8 hydrate of lime in a dry or only slightly damp state. Chlorate of potassa is formed with carbonate of lime and chloride of calcium. The mass is treated with boiling water, which dissolves the chloride of calcium and chlorate of potassa. The latter salt is purified by crystallization. It is stated that other salts of potassa, particularly the sulphate, may be substituted for the carbonate in this process; and that the potassa salt and lime are mixed with hot water when exposed to the chlorine gas.

This salt is anhydrous. It appears in flat crystals of a pearly lustre, of which the forms, according to Brooke, belong to the oblique prismatic system. Its density is 1.989 (Hassenfratz). It has a cooling, disagreeable taste, like that of nitre. According to Gay-Lussac, 100 parts of water dissolve 3⅓ parts of chlorate of potassa at 32°, 6 at 59°, 12 at 95°, 19 at 120.2°, and 60 at 219.2°, the point of ebullition of a saturated solution. This salt fuses readily in a glass retort or tube, enters into ebullition, and discharges oxygen below a red heat. At a certain period in the decomposition, when the mass becomes thick, hyperchlorate of potassa is formed, but ultimately chloride of potassium is the sole residue.

Chlorate of potassa deflagrates with combustibles more violently than the nitrate. A grain or two of it rubbed in a warm mortar with an equal quantity of sulphur, occasions smart explosions, with the formation of sulphurous acid gas. Inclosed with a little phosphorus in paper, and struck by a hammer, it produces a powerful explosion; but this experiment may be attended with danger to the operator from the projection of the flaming phosphorus. A mixture which, when dry, inflames by percussion, and which was applied to lucifer matches, is composed of this salt, sulphur, and charcoal. One of the simplest receipts for this percussion powder consists in washing out the nitre from 10 parts of ordinary gunpowder with water, and mixing the residue intimately, while still humid, with 5¼ parts of chlorate of potassa in an extremely fine powder. This mixture is highly inflammable when dry, and dangerous to preserve in that state. Phosphorus and nitre, however, are now more generally used for these matches (page 315). More chlorate of potassa is employed in the processes of calico-printing, as an oxidizing agent.

Perchlorate of potassa; $KO.ClO_7$; *eq.* 138.5 *or* 1731.25. — Processes for preparing this salt have already been described under perchloric acid (page 342). It is also formed in a strong solution of chlorate of potassa contained in the decomposing cell of a voltaic battery, this salt being deposited in small crystals upon the zincoid, and no oxygen liberated there. It requires 55 parts of water to dissolve it at 59°, but is largely soluble in boiling water. It crystallizes in octohedrons with a square base, which are generally small: they are anhydrous. It deflagrates less strongly with combustibles than the chlorate, loses oxygen at 400°, and is completely decomposed at a red heat, chloride of potassium being left.

Iodate of potassa, $KO.IO_5$; *eq.* 213.36 *or* 2667. — This salt may be formed by neutralizing the chloride of iodine with carbonate of potassa, instead of carbonate of soda (p. 356). It gives small anhydrous crystals, which fuse by heat and lose all their oxygen. Iodic acid likewise forms a biniodate and a teriodate of potassa, according to Serullas. (Annal. de Chim. et de Phys. xliii.) The *biniodate* is obtained by adding an additional proportion of iodic acid to a solution of neutral iodate saturated at a high temperature: it contains an equivalent of water, but may be made anhydrous by a strong heat, according to my own observations. It occurs in prisms with dihedral summits, and requires 75 parts of water at 59° to dissolve it. The *teriodate* is obtained on mixing a strong acid, such as nitric, hydrochloric, or sulphuric, with a hot saturated solution of the neutral iodate, and allowing it to cool slowly. It crystallizes in rhombohedrons, and requires 25 parts of water to dissolve it.

Serullas has observed that the biniodate of potassa has a great disposition to form double salts. A compound with *chloride of potassium*, to which he assigned the formula $KCl+KO.I_2O_{10}$, is obtained on adding a little hydrochloric acid to a solution of iodate of potassa, and allowing the solution to evaporate spontaneously. This salt crystallizes well, but afterwards loses its transparency in the air. It is decomposed by water, and cannot be formed by uniting its constituent salts. Another compound contains bisulphate of potassa: $KO.S_2O_6+KO.I_2O_{10}$. These compounds of iodic acid have also been lately examined by M. Millon.

SECTION II.

SODIUM.

Syn. Natrium. Eq. 23 *or* 287.5; Na.

Davy obtained this metal by the voltaic decomposition of soda, immediately after the discovery of potassium. An intimate mixture of charcoal and carbonate of soda is formed by calcining acetate of soda, from which sodium is commonly prepared, according to the method described for potassium, and with greater facility, owing to the lower affinity of sodium for oxygen. [*See Supplement*, p. 806.]

Sodium is a white metal having the aspect of silver. Its density is 0.972, at 59°, according to Gay-Lussac and Thénard. This metal is so soft, at the usual temperature, that it may be cut with a knife, and yields to the pressure of the fingers; it is quite liquid at 194°. It oxidates spontaneously in the air, although not so quickly as potassium; and when heated nearly to redness takes fire and burns with a yellow flame. Thrown upon water, it oxidates with great vivacity, but without inflaming, evolving hydrogen gas, and forming an alkaline solution of soda. When a few drops only of water are applied to sodium, it easily becomes sufficiently hot to take fire.

As potassium is in some degree characteristic of the vegetable kingdom, so sodium is the alkaline metal of the animal kingdom, its salts being found in all animal fluids. Both of these elements occur in the mineral world; of the two, perhaps potassium is most extensively diffused; felspar, the most common of minerals, containing 12 per cent. of potassa, but from the existence everywhere of a soluble compound of sodium, its chloride, the sources of that element are the more accessible, if not the most abundant.

The anhydrous protoxide of sodium and the peroxide are prepared in the same manner as the corresponding oxides of potassium, which they greatly resemble in properties. The composition of the peroxide of sodium, however, is different, being expressed by the formula $2Na+3O$ (Thénard). It is supposed by M. Millon to be $Na+2O$.

COMPOUNDS OF SODIUM.

Soda; NaO; *eq.* 31 *or* 387.5.—A solution of soda is obtained by decomposing the crystallized carbonate of soda, dissolved in four or five times its weight of water, by means of half its weight of hydrate of lime; the same points being attended to as in the preparation of potassa. A preference is given to this alkali from its cheapness, for most manufacturing purposes, and in the laboratory it may frequently be substituted for potassa, where a caustic alkali is required. On the large scale it is prepared from *salts of soda*, a carbonate containing chloride of sodium and sulphate of soda. The solution of soda is purified from these salts by concentrating it considerably, upon which the foreign salts cease to be soluble in the liquid, and precipitate. (Mr. W. Blythe).

The following table, constructed by Dr. Dalton, exhibits the quantity of caustic soda in solutions of different densities:—

Solution of Caustic Soda.

Density of the Solution.	Alkali per cent.	Density of the Solution.	Alkali per cent.
2·00	77·8	1·40	29·0
1·85	63·6	1·36	26·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·56	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7

The solid hydrate of soda is obtained by evaporating a solution of soda, precisely in the same manner as the corresponding preparation of potassa. It is soluble in all proportions in water and alcohol.

Soda is distinguished from potassa and other bases by several properties:—1st. All its salts are soluble in water, and it is therefore not precipitated by tartaric acid, chloride of platinum, or any other reagent. 2d. With sulphuric acid it affords a salt which crystallizes in large efflorescent prisms, easily recognised as Glauber's salt. 3d. Its salts communicate a rich yellow tint to flame.

Sulphides of sodium.—These compounds so closely resemble the sulphides of potassium as not to require a particular description. The protosulphide of sodium crystallizes from a strong solution in octohedrons. This salt contains water of crystallization; in contact with air it rapidly passes into caustic soda, and the hyposulphite of the same base.

Chloride of sodium, Sea salt, Common salt, NaCl; *eq.* 58.5 *or* 731.25.—Sodium takes fire in chlorine gas, and combining with that element, produces this salt. The chloride of sodium is also formed on neutralizing hydrochloric acid, by soda or its carbonate, and is obtained thus in the greatest purity. Sea-water contains 2.7 per cent. of chloride of sodium, which is the most considerable of its saline constituents: (analysis of sea-water, page 242). Salt is obtained from that source in warm climates, as at St. Ubes, in Portugal, on the coast of the Mediterranean near Marseilles, and other places where spontaneous evaporation proceeds rapidly; the sea-water being retained in shallow basins or canals, on the surface of which a saline crust forms, with the progress of evaporation, which is broken and raked out. Sea-water is also evaporated artificially, by means of culm, or waste coal, as fuel, on some parts of the coast of Britain, but as much for the sake of the *bittern* as of the common salt it affords. The evaporation is not carried to dryness, but when the greater part of the chloride of sodium is deposited in crystals, the mother liquid, which forms the bittern, is drawn off; it is the source of a portion of the Epsom salt and other magnesian preparations of commerce. Other inexhaustible sources of common salt are the beds of sal-gem or rock salt, which occur in several geological formations posterior to the coal, as at Northwich in Cheshire, in Spain, Poland, and many other localities. These beds appear to have been formed by the evaporation of salt lakes without an outlet, in which the saline matter, continually supplied by rivers, had accumulated, till the water being saturated, a deposition of salt took place upon the bottom of the lake. The Dead Sea is such a lake, and the bottom of it is found to be covered with salt. The salt is sometimes sufficiently pure for its ordinary uses, as it is taken from these deposits, but more generally it is coloured brown from an admixture of clay, and requires to be purified by solution and filtration. Instead of sinking a shaft to the bed of the rock salt, and mining it, the superior strata are often pierced by a bore of merely a few inches in diameter, by which water is admitted to the bed, and the brine formed drawn off by a pump and pipe of copper suspended in the same tubular opening.

Chloride of sodium crystallizes from solution in water in cubes, and sometimes from urine and liquids containing phosphates in the allied form of the regular octohedron. Its crystals are anhydrous, but decrepitate when heated, from the expansion of water confined between their plates. According to Fuchs, pure chloride of sodium has exactly the same degree of solubility in hot and cold water, requiring 2.7 parts of water to dissolve it at all temperatures; but it has been proved by Gay-Lussac, and also by Poggiale, that the solubility of this salt increases sensibly, although not considerably, with the temperature. According to Poggiale 100 parts of water dissolve of chloride of sodium 35.52 parts at 32°; 35·87 parts at 57.2 (14° C.); 39.61 parts at 212° (100° C.); and 40.35 parts at 229.46° (109·7° C.), the temperature of ebullition of a saturated solution (Annales de Ch. 3me Sér. viii. 469). Gay-Lussac also makes the boiling point of a saturated solution 229.5°, but that temperature is too high (I believe) for a solution of pure chloride of sodium. When a saturated solution is exposed to a low temperature between 14° and 5°, the salt crystallizes in hexagonal tables, which have two sides larger than the others. Fuchs found these crystals to contain 6, and Mitscherlich 4 equivalents of water. If their temperature is allowed to rise above 14°, they undergo decomposition, and are converted into a congeries of minute cubes, from which water separates.

The little increase of the solubility of chloride of sodium at a high temperature, makes it impossible to crystallize this salt by cooling a hot solution, but Mr. Arrott finds that with the addition of chloride of calcium to the solution, a greater inequality of solubility at high and low temperatures takes place, and a portion of the chloride of sodium crystallizes from a hot saturated solution on cooling. In the evaporation of brine for salt, certain inconveniences attend the deposition of salt from the boiling solution, which Mr. Arrott proposes to obviate by the presence of chloride of calcium.

Pure chloride of sodium has an agreeable saline taste, deliquesces slightly in damp weather, and dissolves largely in rectified spirits, but is very slightly soluble in absolute alcohol. Its density is 2.557 (Mohs). It fuses at a bright red heat, and at a higher temperature rises in vapour. It is immediately decomposed by oil of vitriol, with the evolution of hydrochloric acid. Besides being used as a seasoning for food, chloride of sodium is employed in the preparation of the sulphate and carbonate of soda. When ignited in contact with clay containing oxide of iron, the sodium of this salt becomes soda, and unites with the silica of the clay, while the chlorine combines with iron, and is volatilized as sesquichloride of iron. On this decomposition is founded the mode of communicating the salt-glaze to pottery: a quantity of salt is thrown into the kiln, where it is converted into vapour by the heat, and condensing upon the surface of the pottery causes its vitrification, which is attended with the formation of hydrochloric acid, and of sesquichloride of iron, if sesquioxide of iron be present. When chloride of sodium and silica, both dry, are heated together, no decomposition takes place; but if steam is passed over the mixture, hydrochloric acid is evolved and silicate of soda formed. These decompositions are represented by the following equations:—

$$SiO_3 \text{ and } 3NaCl \text{ and } Fe_2O_3 = 3NaO.SiO_3 \text{ and } Fe_2Cl_3$$
$$SiO_3 \text{ and } NaCl \text{ and } HO = NaO.SiO_3 \text{ and } HCl.$$

The second reaction has not been applied successfully to the preparation of soda from the chloride of sodium, owing, it is said, to the vitrification of the silicate of soda produced, which covers the undecomposed chloride of sodium, and protects it from the steam. Mr. Tilghman substitutes for the silica precipitated alumina, which is made up into balls with the chloride of sodium, and exposed to steam in a reverberatory furnace at an elevated temperature. Hydrochloric acid escapes, and an aluminate of soda is formed, which may be decomposed, when cold, by dry carbonic acid; the carbonate of soda is dissolved out by water; the alumina is made up again into balls with chloride of sodium, to be ignited and decomposed by steam as before.

The bromide and iodide of sodium crystallize in cubes, and resemble in properties the corresponding compounds of potassium.

FIG. 172.

SALTS OF OXIDE OF SODIUM.

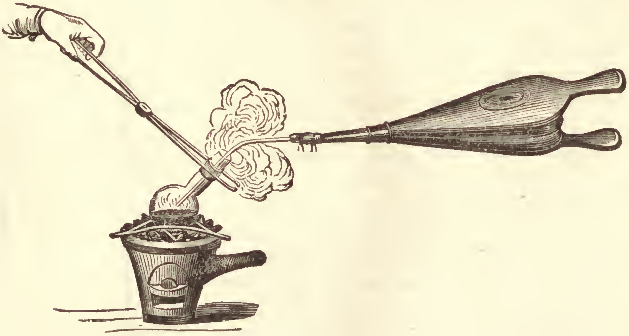
Carbonate of soda; $NaO.CO_2+10HO$; *eq.* 53+90, *or* 662.5+1125.—This useful salt is found nearly pure in commerce, in large crystals, which effloresce when exposed to air. These crystals contain 10 equivalents of water, and consist, in 100 parts, of 21.81 soda, 15.43 carbonic acid, and 62.76 water. According to Dr. Thomson, they generally contain about ½ per cent. of sulphate of soda as an accidental impurity: they belong to the oblique prismatic system. Their density is 1.623: 100 parts of water dissolve 20.64 of the crystals at 58.25°, and more than an equal weight at the boiling temperature (Dr. Thomson). In warm weather, the carbonate of soda sometimes crystallizes in another form, which is not efflorescent, and of which the proportion of water is 8 equivalents. The ordinary crystals, by efflorescing in dry air, are reduced to a hydrate of 5 equivalents of water, $NaO.CO_2+5HO$. The same hydrate appears when a solution of carbonate of soda is made to crystallize at 93° (34° C.), in crystals derived from an octohedron with a square base. Again, a solution of this salt evaporated between 158° and 176° (70° and 80° C.), deposits quadrilateral crystals, containing 1 equivalent of water, or 14.77 per cent. Carbonate of soda, therefore, appears to be capable of forming four definite hydrates, containing HO, 5HO, 8HO, and 10HO. The density of the anhydrous salt is 2.509 (Filhol).

The solubility of the carbonate of soda, supposed to be anhydrous, at various temperatures, was observed by M. Poggiale to be as follows:—

100	parts of water at	32° (0° C.)	dissolve	7.08	of carbonate of soda.
100	" "	50° (10° C.)	"	16.66	" "
100	" "	68° (20° C.)	"	25.83	" "
100	" "	86° (30° C.)	"	35.90	" "
100	" "	219.2° (104° C.)	"	48.50	" "

To obtain such determinations of the solubility of a salt at a given temperature, water is kept in contact with a considerable excess of the salt in the state of powder for at least half an hour, at the fixed temperature, with occasional agitation. About two ounces of the solution is then transformed into a light glass flask (fig. 173), and after being accurately weighed, is evaporated either over the gas, or by a small furnace, taking care to hold the neck at an angle of 45°, to avoid drops of fluid being thrown out by the ebullition. After the salt is dry, the heat is still continued, to expel the water of crystallization, the escape of the latter being promoted by blowing air gently into the flask while hot by means of bellows having a bent glass tube attached to the nozzle. [*See Supplement*, p. 807.]

Fig. 173.



This salt has a disagreeable alkaline taste. When heated, it undergoes the watery fusion; its water is soon dissipated, and a white anhydrous salt remains, which again becomes liquid at a red heat, undergoing then the igneous fusion, and by a greater heat it loses no carbonic acid. A mixture of carbonates of potassa and soda is more fusible than either salt separately.

Carbonate of soda is decomposed at a bright red heat by the vapour of water, which disengages all the carbonic acid, and produces hydrate of soda, NaO.HO. The carbon of its acid is also set at liberty by phosphorus at a hign temperature, and the phosphate of soda formed. Lime, baryta, strontia, and magnesia, decompose a solution of carbonate of soda, assuming its carbonic acid and liberating soda.

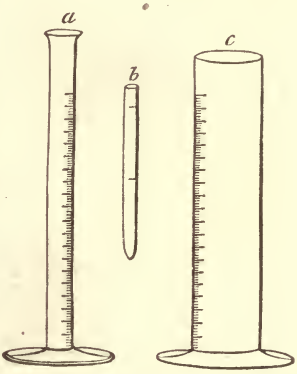
Carbonate of soda is manufactured by a process which will be described immediately under the head of sulphate of soda. Much of the carbonate of commerce is not crystallized, but simply evaporated to dryness, and is then known as *salts of soda*, *soda-salt*, or *soda-ash.* In this form it generally contains chloride of sodium, sulphate of soda, hydrate of soda, and often insoluble matter, and varies considerably in value. The soda which is caustic, and that in combination with carbonic acid alone of the acids, are available in the application of the salt as an alkaline substance. The pure anhydrous carbonate of soda consists of 58.58 soda and 41.42 carbonic acid, and the best soda-salts of commerce contain from 50 to 53 per cent. of available soda. The operation of ascertaining the proportion of alkali in these salts, and in other forms of the carbonate of soda, is a process of importance from its frequent occurrence, and of high interest and value as a general method of analysis of easy execution, and applicable to a great variety of substances. I shall therefore describe minutely the mode of conducting it.

ALKALIMETRY.

The experiment is, to find how many measures of a diluted acid are required to destroy the alkaline reaction of, and to neutralize 100 grains of a specimen of soda-salt. (1.) The acid is measured in the alkalimeter, which is a straight glass tube, or very narrow jar, with a lip (fig. 174), about 5-8ths of an inch in width, and 14 or 15 inches in height, generally mounted upon a foot, which is by no means advantageous, as *a*, (fig. 175), capable of containing at least 1000 grs. of water. It is graduated into 100 parts, each of which holds ten grains of water. In the operation of dividing such an instrument, it is more convenient to use measures of mercury than water,—135.68 grains of mercury being in bulk equal to 10 grains of water, 678.40 grains will be equal to 50 grains of water. A unit measure may be formed of a pipette, *b*, made to hold the last quantity of mercury, into which the metal is poured, the opening at the point of the pipette being closed by the finger, and the height of the mercury in the tube marked by a scratch on the glass made by a triangular file. The bulk of twice that quantity of mercury, or 100 water grain measures, may likewise be marked upon the tube. The former quantity of mercury is then decanted from the tube into the alkalimeter to be graduated, and a scratch made upon the latter at the mercury surface: this is 5 of the 10-grain water measures. Another measure is added, and its height marked; and the same repeated till 20 measures of mercury in all have been added, which are 100 ten-grain water measures. The subdivision of each of these measures into 5 is best made by the eye, and is also marked on the alkalimeter. The divisions are lastly numbered, 0, 5, 10, &c., counting from above downwards, and terminating with 100 on the sole of the instrument. Several alkalimeters may be graduated at the same time, with little more trouble than one, the measured quantities of mercury being transferred from one to the others in succession.

Fig. 174.

Fig. 175.



(2.) To form the test acid, 4 ounces of oil of vitriol are diluted with 20 ounces of water; or larger quantities of acid and water are mixed in these proportions. About three-fourths of an ounce of bicarbonate of soda is heated strongly by a lamp for an hour, to obtain pure carbonate of soda; of which 171 grains are immediately weighed; that quantity, or more properly 170.6 grains, containing 100 grains of soda. This portion of carbonate of soda is dissolved in 4 or 5 ounces of hot water, contained in a basin, and kept in a state of gentle ebullition; and the alkalimeter is filled up to 0 with the dilute acid. The measured acid is poured gradually into the soda solution, till the action of the latter upon test-paper ceases to be alkaline, and becomes distinctly acid, and the measures of acid necessary to produce that change accurately observed. The last portions of the acid must be carefully added by a single drop at a time, which is most easily done by using a short glass rod to conduct the stream of acid from the lip of the alkalimeter. It may probably require about 90 measures. But it is convenient to have the acid exactly of the strength at which 100 measures of it saturate 100 grains of soda. A plain cylindrical jar, *c*, of which the capacity is about a pint and a half, is graduated into 100 parts, each containing 100 grain measures of water, or ten times as much as the divisions of the alkalimeter. The divisions of this jar, however, are numbered from the bottom upwards, as is usual in measures of capacity. This jar is filled up with the dilute acid to the extent of 90, or whatever number of the alkalimeter divisions of acid were found to neutralize 100 grains of soda; and *water* is added to make up the acid liquid to 100 measures. Such is the test acid, of which 100 alkalimeter measures neutralize, and are equivalent to, 100 grains of soda; or 1 measure of acid to 1 grain of soda. It is transferred to a stock bottle. The remainder of the original dilute acid is diluted with water to an equal extent, in the same instrument, and added to the bottle. The density of this acid is 1.0995 or 1.0998, which is sensibly the same as 1.1. The protohydrate of sulphuric acid diluted with 5½ times its weight of water, gives this test acid exactly; but as oil of vitriol varies in strength, it is better to form the test acid exactly; but as oil of vitriol varies in strength, it is better to form the test acid in the manner described than to trust to that mixture. Twenty-two measures of the test acid should neutralize 100 grains of cr. carbonate of soda; and 58½ measures, 100 grains of pure anhydrous carbonate of soda.

(3.) In applying the test-acid, it is poured from the alkalimeter, as before, upon 100 grains of the soda-salt to be tested, dissolved in two or three ounces of hot water, the liquid being well stirred by a glass rod after each addition of acid. The salt contains so many grains of soda as it requires measures of acid to neutralize it; and, therefore, so much alkali per cent. The first trial, however, should only be considered an approximation, as much greater accuracy will be obtained on a repetition of it. The experiment is often made in the cold, but it is very advantageous to have the alkaline solution in a basin, in which it is heated and evaporated during the addition of the test-acid. The indications of the test-paper then become greatly more clear and decisive, both from the expulsion of the carbonic acid and the concentration of the solution. With such precautions the proportion of soda may be determined to 0.1 grain in 100 grains of salt, and an alkalimetrical determination, made in a few minutes, is not inferior in precision to an ordinary analysis.

If the soda-salt is mixed with insoluble matter, its solution must be filtered before the test-acid is applied to it. In examining a soda-salt which blackens salts of lead, and contains carbonate of soda with sulphide of sodium and hyposulphite of soda, 100 grains are tested as above, and the whole alkali in the salts thus determined. A neutral solution of chloride of calcium is also added in excess to the solution of a second hundred grains, by which the carbonate of soda is converted into chloride of sodium, while carbonate of lime precipitates. The filtered liquid is still alkaline, and contains all the sulphide of sodium and hyposulphite of soda; the quantity of soda corresponding with which is ascertained by means of the test-acid. This quantity is to be deducted from the whole quantity of alkali observed in the first experiment.

Borax may be analysed by the same test-acid, and will be found, when pure, to contain 16.37 per cent. of soda. The carbonates of potassa may also be examined by the same means; but the per centage of alkali must then be estimated higher than the measures of acid neutralized, in the proportion of the equivalent of soda to that of potassa, which are to each other as 31 to 47.

The test-paper employed in alkalimetry must be delicate. It should be prepared on purpose, by applying a filtered infusion of litmus several times to good letter-paper (not unsized paper), and drying it after each immersion, till the paper is of a distinct but not deep purple colour. If the test-acid be added to the alkaline solution in the cold, the operator must make himself familiar with the difference between the slight reddening of his test-paper by carbonic acid which is disengaged, and the unequivocal reddening which is produced by the smallest quantity of a strong acid. The former is a purple or wine-red tint; the latter a pale or yellow red, without blue, like the skin of an onion.

Method of Gay-Lussac.—The directions for proceeding given by M. Gay-Lussac are recommended by the general utility of the French measures employed for scientific purposes. It is commercial potassa which is supposed to be examined, and its value is expressed in anhydrous oxide of potassium.

The acid employed is the sulphuric, as before, of which 5 grammes at its maximum of concentration, that is, the acid $HO.SO_3$, are taken as a unit. This quantity of acid is diluted with water, so that the mixture occupies fifty cubic centimeters, or one hundred half cubic centimeters.[1] It is capable of neutralizing 4.816 grammes of pure potassa, and one-half cubic centimeter of the dilute acid will consequently indicate 0.04816 gramme of potassa.

To prepare the *normal acid fluid*, as the test-acid is called, it is necessary to have the pure monohydrated sulphuric acid. The acid sold as distilled sulphuric acid is sufficiently free from fixed impurities, but generally contains a little water in excess. By evaporating off one-fourth of this acid, the remaining three-fourths are left of the maximum degree of concentration. One hundred grammes of the monohydrated sulphuric acid are accurately weighed in a small glass bottle. A thin glass flask is also provided, which holds a liter of water when filled to a mark on the neck. The sulphuric acid already weighed is added in a gradual manner to this flask, about half filled with water at first, a circular motion being given to the vessel in order to mix the liquids rapidly. The acid bottle is well rinsed out with water, which is added to the flask; and when the whole cools, more water is added to fill up the flask to the mark on the neck. The normal acid fluid, thus prepared, should be preserved for use in a well-stopped bottle.

In making an examination of commercial potashes, a fair sample of the mass is first taken, and reduced to powder; of this, 48.16 grammes are accurately weighed out, and dissolved in a quantity of water, so that the volume of the solution is exactly half a liter. If one-tenth of this liquid be taken, that is, fifty cubic centimeters, we shall of course have the quantity which contains 4.816 grammes of the potashes. To draw off this portion conveniently, a pipette is used (fig. 176), which holds fifty cubic centimeters when filled up to a mark *a* on its stem. The pipette is emptied into a plain glass jar, the last drop of liquid being made to flow out by blowing into the pipette. A sufficiently distinct blue tint is given to the liquid in the jar by the addition of a few drops of an infusion of litmus, and the jar placed upon a sheet of white letter-paper, in order to observe the changes of colour afterwards with more facility.

FIG. 176.

To measure the normal acid fluid, a glass tube of the form fig. 177 is used, 12 or 14 millimeters in internal diameter, which is called a *burette*. It is divided into half cubic centimeters, and the divisions marked on the large tube in an inverse order, as in the former alkalimeter. The beak may be greased below the aperture, to prevent the liquid running

FIG. 177.

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[1] The Gramme is 15.4336 grains; the Cubic Centimeter, 0.06103 English cubic inch; the Liter or 1000 cubic centimeters, 61.03 cubic inches, 0.22017 English imperial gallon, or 1.76133 pint.

down the outside of the glass. The acid is poured from the burette, filled to the division 0, into the jar containing the potassa-solution, the liquid in the latter being constantly stirred. The change to the wine-colour is first observed, and the addition of acid is afterwards continued with the greatest caution, drop by drop, till the liquid assumes at once the onion-skin red. A few drops of acid in excess are inevitably added, owing to the slowness of the action of the last portions of acid upon the colouring matter. The number of these drops in excess is discovered by drawing a line with the liquid upon a slip of blue litmus paper, after the addition of each drop. The lines become red after the lapse of some time, where the acid is in excess, and give the number of drops to be deducted; of these, five are in general equivalent to one measure of the burette. The quantity of potassa is calculated from the measures of normal acid fluid prepared, each measure representing 0.04816 gramme of potassa, as already stated.

The chief objection to the practice of this method is the delicacy, and in some degree uncertainty, of the mode of determining the number of drops of acid always added in excess. This difficulty is best avoided, I believe, by operating upon the alkaline solution while hot and undergoing evaporation, as directed in the preceding method of alkalimetry.[1]

The object of an alkalimetrical process may also be obtained by determining the quantity of carbonic acid in a specimen of soda-ash or potashes. The quantity of carbonic acid is ascertained by decomposing the carbonate by sulphuric acid, and observing the loss of weight occasioned by the escape of the gas. The evolution of hydrosulphuric acid gas at the same time, by the decomposition of sulphide of sodium, is prevented by adding a little bichromate of potassa to the sulphuric acid, so as to oxidize the former acid gas. For every equivalent of carbonic acid, or 22 parts, an equivalent quantity of soda or potassa is allowed to be present; namely, 31 parts of soda or 47 parts of potassa. The process may be conducted by means of the well-devised arrangements of Dr. Will, described in works upon Analytical Chemistry. It would, however, be a subject of regret if this latter method should be allowed to supersede the use of normal fluids and the burette, which are capable of being usefully applied in numerous other investigations besides alkalimetry, and, in fact, form the basis of an interesting department of chemical analysis.

Bicarbonate of soda; $HO.CO_2 + NaO.CO_2$; 84 *or* 1050. — This salt is formed when a stream of carbonic acid gas is transmitted through a saturated solution of the neutral carbonate; it is then deposited as a farinaceous powder, but may be obtained in crystals from a weaker solution, which are rectangular prisms. But it is generally prepared on the large scale by exposing the crystals of neutral carbonate, placed on trays in a wooden case, to an atmosphere of carbonic acid gas: the matter then changes entirely into bicarbonate, which appears in amorphous and opaque masses. One hundred parts of water dissolve of it 10.04 parts at 50° (10° C.) and 16.69 parts at 158° (70° C.), according to M. Poggiale. Although containing two equivalents of acid, this salt is alkaline to test-paper, but its taste is much less unpleasant than the neutral carbonate, and indeed is scarcely perceived when mixed with a little common salt. The crystallized salt is permanent in dry air, but its solution loses carbonic acid, slowly at the temperature of the air, and rapidly above 160°, passing into the state of sesquicarbonate, and ultimately of neutral carbonate. A solution of bicarbonate of soda does not produce a precipitate in salts of magnesia in the cold, nor does it disturb immediately a solution of chloride of mercury; by which properties it is distinguished from the neutral carbonate.

The bicarbonate of soda is obtained otherwise by an interesting reaction. Equal weights are taken of common salt and of the carbonate of ammonia of the shops, which is chiefly bicarbonate; the former is dissolved in three times its weight of

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[1] The apparatus and methods of alkalimetry have received much attention from Mr Griffin. His improved apparatus and test-paper may be procured at the Chemical Museum, 53, Baker Street.

water, and the latter added in the state of fine powder to this solution, the whole stirred well together, and allowed to stand for some hours. The bicarbonate of oxide of ammonium present reacts upon chloride of sodium, producing the more sparingly soluble bicarbonate of soda, which precipitates in crystalline grains and causes the liquid to become thick, with chloride of ammonium (sal-ammoniac), which remains in solution:—

$$HO.CO_2+NH_4O.CO_2 \text{ and } NaCl=$$
$$HO.CO_2+NaO.CO_2 \text{ and } NH_4Cl.$$

The solid bicarbonate of soda is separated from the liquid by pressure in a screw press; but retains a portion of chloride of sodium. Messrs. Hemming and Dyer, who first observed this reaction, proposed it as a process for obtaining carbonate of soda from common salt.

Sesquicarbonate of soda; $2NaO+3CO_2+4HO$; 164 *or* 2050.—This salt presents itself occasionally in small prismatic crystals, but cannot be prepared at pleasure. It is unalterable in the air, but is decomposed in the dry state by a less degree of heat than the bicarbonate, notwithstanding its containing a smaller excess of carbonic acid. The theoretical carbonate of water, supposed to resemble the carbonate of magnesia, will be $HO.CO_2+HO+2HO$; which gives the salt in question, if the last 2HO are replaced by two proportions of protohydrated carbonate of soda. Substitutions of this character appear to be common in the formation of double carbonates and oxalates. The bicarbonate of potassa may be formed by the substitution of carbonate of potassa for the first HO, in the same carbonate of water, while the other 2HO disappear. The sesquicarbonate of soda occurs native in several places, particularly on the banks of the lakes of Soda in the province of Sukena, in Africa, whence it is exported under the name of *Trona;* in Egypt, Hungary, and in Mexico, and has the same proportion of water as the artificial salt.

Double carbonate of potassa and soda.—The carbonates of potassa and soda unite readily by fusion. A compound was also obtained by M. Margueritte, in transparent crystals, by submitting a solution of the two carbonates, in different proportions, to evaporation, of which the formula is $2(NaO.CO_2)+(KO.CO_2)+18HO$. These crystals may be dissolved without injury in a solution of carbonate of potassa, but when dissolved in pure water they are in great part decomposed, and allow crystals of carbonate of soda to be deposited. This double salt may be analysed by evaporating to dryness, after first adding hydrochloric acid, to convert the bases into chlorides of potassium and sodium, and then precipitating the former by means of bichloride of platinum, as described at page 373.

Sulphite of soda; $NaO.SO_2+10HO$; 63 + 90, *or* 787.5 + 1125.—This salt crystallizes in oblique prisms, and is efflorescent like the sulphate of soda, which it much resembles. Its taste is sulphureous, and its reaction feebly alkaline. When heated strongly in a close vessel, it gives sulphate of soda mixed with sulphide of sodium. It is prepared by passing a stream of sulphurous acid through a solution of the carbonate of soda (page 294), or on the large scale by exposing the crystals of carbonate of soda, moistened, to the vapour of burning sulphur. This salt, and also the sulphite of lime, are much employed as an *antichlore,* or to remove the last traces of chlorine from bleached cloth and the pulp of paper. A bisulphite of soda also exists, which appears in irregular and opaque crystals.

Hyposulphite of soda; $NaO.S_2O_2+5HO$; 79 + 45, *or* 987.5 + 562.5.—This salt, of which the preparation and some of the properties have already been described (page 303), is inodorous, persistent in air, very soluble in water, and insoluble in alcohol. It crystallizes in large rhomboidal prisms, terminated by oblique faces, of which the acute angles are replaced by planes. When heated in a covered vessel, it first loses its water, and then undergoes decomposition, and is resolved into sulphate of soda and pentasulphide of sodium. The hyposulphite of soda readily dissolves chloride of silver, forming a double salt of soda and oxide of silver, which has an intensely sweet taste. It also dissolves the red oxide of mercury easily, forming a double salt, which readily decomposes with deposition of sulphide of mercury. With chloride of gold, it gives rise to the formation of chloride of sodium, tetrathionate of soda, and a double hyposulphite of soda and oxide of gold, of which the formula is

$$Au_2O.S_2O_2+3(NaO.S_2O_2)+4HO$$ (Fordos and Gelis).

The use of this last salt is recommended for fixing the daguerréotype image.

Sulphate of soda, Glauber's salt; $NaO.SO_3+10HO$; 71+90, *or* 887.5+1125.—This salt occurs crystallized in nature, and also dissolved in mineral waters, and is formed on neutralizing carbonate of soda by sulphuric acid. But it is more generally prepared by decomposing common salt with sulphuric acid, as in the process for hydrochloric acid (page 335). The sulphate of soda crystallizes readily in long prisms, of which the sides are often channelled, which have a cooling and bitter taste, and contain 55.76 per cent. of water, or 10 equivalents; in which they fuse by a slight elevation of temperature, and which they lose entirely by efflorescence in dry air even at 40°. At 32°, 100 parts of water dissolve 5.02 parts of anhydrous sulphate of soda, 16.73 parts at 64.2° (17.91° C.), 50.65 parts at 91°, which is the temperature of maximum solubility of this salt, and 42.65 parts at the boiling temperature of a saturated solution, which is 217.6° (103.1° C.), as observed by Gay-Lussac. In a supersaturated solution of this salt (page 239), crystals are sometimes slowly deposited, which are different in form and harder than Glauber's salt; they are long prisms with rhombic bases, and contain 8 equivalents of water, or possibly only 7 equivalents (Loewel, Annal. de Ch. et de Phys. 3 sér. xxix. 62; or Chem. Soc. Quart. Journ. iii., 164). [*See Supplement*, p. 807.]

M. Loewel finds these crystals to have a greater solubility than the ten-atom hydrate. The sulphate of soda no doubt exists in the supersaturated solution as eight-atom hydrate, and the salt is induced to crystallize by causes which make it to assume two additional equivalents of water, and form the less soluble hydrate. It is proved that the action of air in causing crystallization is not from its pressure (Gay-Lussac, Annal. de Ch. et de Ph. 2 sér. ii. 296); but, as I have shown, from the solubility of air in the saline solution, carbonic acid exceeding air in activity (Edinb. Trans. xi. 114). Loewel observes, among other curious circumstances, that a rod of glass or metal, which determines the formation of the ten-atom hydrate when plunged into the supersaturated solution, loses this property if it is left in contact with water for twelve hours, or if it has been previously heated to between 40° and 100° C., and continues incapable of inducing crystallization for ten days or a fortnight at the ordinary temperature, if preserved from free contact with the air. I had previously put up clean glass beads into supersaturated solutions contained in jars inverted over mercury, without determining crystallization, and would ascribe the action of the glass surface to adhering soluble matter, rather than the molecular condition of the glass, as supposed by M. Loewel.

A saturated solution of sulphate of soda, kept at a temperature between 91° and 104°, affords octohedral crystals with a rhombic base, which are anhydrous. They are isomorphous with the hypermanganate of baryta. Their density is 2.642. The anhydrous salt fuses at a bright red heat, without loss of acid. Sulphate of soda was at one time the saline aperient in general use, but is now superseded by sulphate of magnesia. It is still, however, occasionally associated with the tartrate of potassa and soda, in Seidlitz powders.

The crystallized sulphate of soda dissolves freely in hydrochloric acid, or in dilute sulphuric acid, and produces a great degree of cold, by which water may easily be frozen in summer. A suitable apparatus for this purpose consists of a hollow cylinder C C (figs. 178 and 179), intended for the reception of the freezing mixture, itself surrounded by a space to contain the water to be frozen, having the external opening *u*, and the whole protected by a double casing, B B, filled with cotton or tow to prevent access of heat. The cylinder A is hollow, and may also have water placed in it to be frozen. This cylinder is turned on a pivot by the handle above,

Fig. 178.

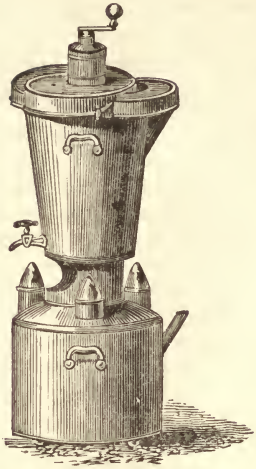
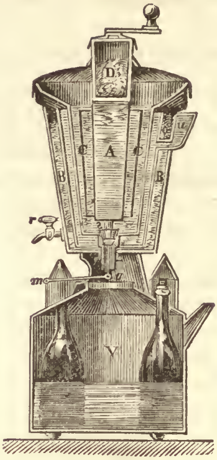


Fig. 179.



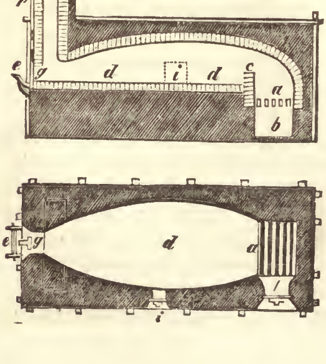
and has projections or vanes, by which the salt and acid are conveniently agitated The upper part, D, of this cylinder is filled with a non-conducting material. The freezing mixture is added in charges of about 3 pounds of pulverized sulphate of soda, and 2 pound measures of hydrochloric acid, at a time; which are repeated after ten minutes, and the stopcock opened to allow the acid solution to flow into the vessel V below, where its low temperature may be further employed to cool wine or other beverages. With 12 pounds of sulphate of soda, and about 10 pounds of acid, from 10 to 12 pounds of ice may be formed in the course of an hour in this manner.

The anhydrous sulphate of soda also forms the mineral *Thenardite,* which was discovered by M. Casasecu in the neighbourhood of Madrid.

PREPARATION OF CARBONATE OF SODA FROM THE SULPHATE.

The sulphate of soda is chiefly formed as a step in the process of preparing soda from common salt. The same manufacture gives rise to the preparation of large quantities of sulphuric acid, of which 80 pounds are required for 100 pounds of salt. From the last, upwards of 50,000 tons of *soda-ash*, and 20,000 tons of crystallized carbonate of soda, were manufactured in 1838; and the production has since greatly increased.

Fig. 180.



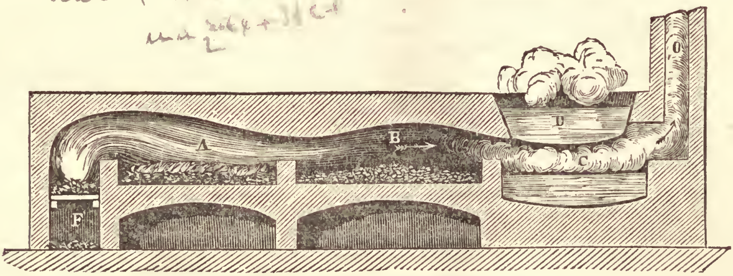
A reverberatory furnace is employed in soda-making and various other chemical manufactures, to afford the means of exposing a considerable quantity of materials to a strong heat, of which a perpendicular and a horizontal section are given in fig. 180. It consists of a fire-place, *a*, in which the fuel is burned, of which *b* is the ash-pit, with a horizontal flue expanding into a small chamber or oven, *d d*, which is raised to a strong red heat by the reverberation on its walls of the flame or heated air from the fire, on its passage to the chimney. The matters to be heated are placed upon the floor of this chamber. It has an opening, *i*, in the side, for the introduction of materials, and another opening, *g*, at the end most distant from the fire. The chimney is provided with a damper, *p*, by which the draught is regulated.

(1.) The sulphate of soda is prepared by throwing 600 pounds of common salt into the chamber of the furnace, already well heated, and running down upon it, from an opening in the roof, an equal weight of sulphuric acid of density 1.600, in a moderate stream. Hydrochloric acid is disengaged and carried up the chimney, and the conversion of the salt into sulphate of soda is completed in four hours. (2.) The sulphate thus prepared is reduced to powder and 100 parts of it mixed with 103 parts of ground chalk, and 62 parts of small coal ground and sifted. This mixture is introduced into a very hot reverberatory furnace, about two hundred weight at a time. It is frequently stirred until it is uniformly heated. In about an hour it fuses; it is then well stirred for about five minutes, and drawn out with a rake into a cast-iron trough, in which is is allowed to cool and solidify. This is called ball soda, or black-ash, and contains about 22 per cent. of alkali. (3.) To separate the salts from insoluble matter, the cake of ball soda, when cold, is broken up, put into vats, and covered by warm water. In six hours the solution is drawn off from below, and the washing repeated about eight times, to extract all the soluble matter. These liquors being mixed together are boiled down to dryness, and afford a salt which is principally carbonate of soda, with a little caustic soda and sulphide of sodium. (4.) For the purpose of getting rid of the sulphur, the salt is mixed with one-fourth of its bulk of sawdust, and exposed to a low red heat in a reverberatory furnace for about 4 hours, which converts the caustic soda into carbonate, while the sulphur also is carried off. This product contains about 50 per cent. of alkali, and forms the soda-salt of best quality. (5.) If the crystallized carbonate is required, the last salt is dissolved in water, allowed to settle, and the clear liquid boiled down until a pellicle appears on its surface. The solution is then run into shallow boxes of cast-iron, to crystallize in a cool place; and after standing for a week the mother liquor is drawn off, the crystals drained, and broken up for the market. (6.) The mother liquor, which contains the foreign salts, is evaporated to dryness, for a soda-salt, which serves for soap or glass making, and contains about 30 per cent. of alkali.

In fig. 181, a soda-furnace is represented, consisting of two compartments: the first, A, in which the sulphate of soda is decomposed, and the second, B, in which sulphuric acid is applied to the chloride of sodium, and the sulphate of soda formed. The heat from the furnace is further economized by being applied to evaporate solutions of carbonate of soda in C and D.

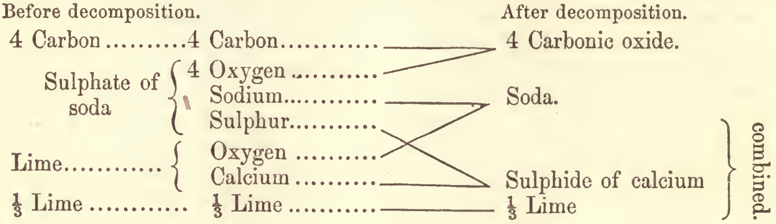
FIG. 181.

[illegible] + 1/2 [illegible]
[illegible]



The most essential part of this process is the fusion of sulphate of soda with coal and carbonate of lime: by the first, the sulphate is converted into sulphide of sodium (page 383); and by the second, the sulphide of sodium is converted into carbonate of soda. These changes may be effected separately to a considerable extent, but not completely, by calcining the sulphate at a higher temperature with coal and carbonate of lime in succession. The lime becomes at the same time sulphide of calcium, or it is more generally supposed to form an oxi-sulphide of calcium, $3CaS.CaO$, a compound which would destroy the carbonate of soda, if it was dissolved along with that salt, in the subsequent lixiviation of the ball soda. But the sulphide of calcium being nearly insoluble of itself, or rendered entirely so by its combination with lime, does not dissolve to a sensible extent in the experiment. The application, however, of very hot water to the ball soda is to be avoided. The following diagram is used to represent the chemical changes in this process, supposing for simplicity that charcoal is employed instead of coal, and lime instead of its carbonate; the numbers denoting equivalents:—

REACTION IN THE SODA PROCESS.



Mr. Gossage considers the additional ⅓ equiv. of lime as superfluous, although not injurious in the process. The soda derives carbonic acid from the carbonate of lime or from the gases of the fire, and is therefore entirely carbonate. No hydrate of soda is dissolved out of the ball soda by alcohol, but a portion of the carbonate appears often to become caustic by the action of the caustic lime, in the subsequent lixiviation.[1]

The insoluble sulphide of calcium of this process is known as soda-waste. It is

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[1] The analysis, by Mr. F Claudet in my laboratory, of a specimen of black-ash from Birmingham, in which a minimum of lime appears to have been used, gave the following results:—

Soluble.	Carbonate of Soda	35.42	
	Sulphide of Sodium	1.45	
	Sulphate of Soda	.78	
	Chloride of Sodium	2.62	
	Silicic acid	.58	
	Oxide of Iron, Alumina	.15	
Insoluble.	Sulphide of Calcium	32.90	= Sulphur 14.6 Calcium 18.9
	Carbonate of Lime	3.73	= Lime 2.09
	Magnesia	.56	
	Oxide of Iron	1.98	
	Alumina	3.59	
	Sand and Silicic acid	4.95	
	Charcoal	10.57	
	Water	.72	
		100.00	

The lime found is not in quantity sufficient to form the oxi-sulphide of calcium, $3CaS.CaO$; confirming the view of the process taken by Mr. Gossage. No hydrate of soda, or sulphide of sodium, was dissolved out of this black-ash by alcohol. The portion of the latter salt obtained in the analysis appeared to be the result of over-washing; the sulphide of calcium having a tendency to pass into lime and the soluble hydrosulphate of sulphide of calcium, which decompose a portion of the carbonate of soda. Although this important process has been much studied, its theory is still incomplete. The furnacing of the sulphate of soda is promoted by aqueous vapour, and a loss of sulphur occurs in a way which is not understood. See the papers of Mr. J. Brown (Phil. Mag. xxxiv. 15), of M. B. Unger (Ann. Ch. Pharm., lxi. lxiii. and lxvii.), and the Annual Report on the Progress of Chemistry of Liebig and Kopp, edited by Hoffmann and De la Rue, ii. 292, 1847–48.

not merely valueless, but troublesome to the manufacturer. But the attempt has been made to turn it to account as a source of sulphur. As means are now taken to condense the hydrochloric acid, formerly sent up the chimney, this acid is applied to the soda-waste, from which it disengages hydrochloric and carbonic acids. But hydrochloric acid is not produced, in the soda process, in adequate quantity for this application of it, and the carbonic acid evolved with the hydrosulphuric acid might interfere with the combustion of the latter. These difficulties, however, are in a great degree removed by the discovery of Mr. Gossage, that sulphide of calcium, when moistened with water, is decomposed easily and completely by a single equivalent of carbonic acid. Hence the application of hydrochloric acid to the waste may be made, with the evolution of nothing but hydrosulphuric acid; and the deficiency in the quantity of hydrochloric acid may be made up by a supply of carbonic acid, to be applied to the waste, from any other source. The hydrosulphuric acid would be burned, instead of sulphur, in the leaden chamber, to produce sulphuric acid.

Many changes have been proposed upon the soda process. Sulphate of iron, produced by the oxidation of iron-pyrites, is a cheap salt, and may be applied to convert chloride of sodium into sulphate of soda.—(1.) By igniting a mixture of these salts in a reverberatory furnace, when sulphate of soda, sesquioxide of iron, and volatile sesquichloride of iron are produced. (2.) By dissolving the salts together in water, and allowing the solution to fall to a low temperature, when sulphate of soda crystallizes, and chloride of iron remains in solution (Mr. Phillips); or (3.) By concentrating the last solution at the boiling-point, when the same decomposition occurs, anhydrous sulphate of soda precipitates, and may be raked out of the liquor. The roasting of bisulphide of iron with common salt in a reverberatory furnace may also be made to furnish sulphate of soda. Sulphate of magnesia has been substituted for sulphate of iron, in these three modes of application; but the unavoidable formation of double salts of magnesia and soda makes the separation of the sulphate of soda always imperfect. It has been proposed, instead of furnacing the sulphate of soda, to decompose it by caustic baryta, or by strontia, the last earth being procured by Mr. Tilghmann, for this application of it, by decomposing the native sulphate of strontia from Bristol, by a current of steam at a red heat. Such a process should also furnish the sulphuric acid required to decompose chloride of sodium and form sulphate of soda. Chloride of sodium may also be decomposed by moistening and rubbing it in a mortar with 4 or 6 times its weight of litharge, when an oxichloride of lead is formed, and caustic soda liberated. The decomposition of chloride of sodium by the carbonate of ammonia, with formation of bicarbonate of soda, has already been noticed (page 389). It appears, however, that the soda-process first described, which was invented towards the end of the last century by Leblanc, is still generally preferred to all others.

The old sources of carbonate of soda, namely *barilla*, or the ashes of the salsola soda, which is cultivated on the coasts of the Mediterranean, and *kelp*, the ashes of sea-weeds, have ceased to be of importance, at least in England. Barilla contains about 18, and kelp about 2 per cent. of alkali.

Bisulphate of soda, $HO.SO_3 + NaO.SO_3$; 120 *or* 1500. This salt is obtained in large crystals on adding an equivalent of oil of vitriol to sulphate of soda, and evaporating the solution till it attains the degree of concentration necessary for crystallization. If half an equivalent only of oil of vitriol is added, a *sesquisulphate of soda* is obtained in fine crystals, according to Mitscherlich. The ordinary bisulphate of soda contains basic water, but it may be rendered anhydrous by a degree of heat approaching to redness. The salt thus obtained is a true bisulphate of soda, and gives anhydrous sulphuric acid when distilled at a red heat.

Nitrate of soda; $NaO.NO_5$; 85 *or* 1062.5.—This salt crystallizes in the rhomboidal form of calc-spar; density 2.260. It is soluble in twice its weight of water, and has a tendency to deliquesce in damp air. It burns much slower with combustibles than nitrate of potassa, and cannot therefore be substituted for that salt in the manufacture of gunpowder. It is now generally had recourse to, as the source of nitric acid, and is also largely used in agriculture. Nitrate of soda is found abundantly in the soil of some parts of India; and it forms a thin but very extensive bed covered by clay at Atacama in Peru, from which it is exported in great quantity.

Chlorate of soda ($NaO.ClO_5$) is formed by mixing strong solutions of bitartrate of soda and chlorate of potassa, when the bitartrate of potassa precipitates, and the chlorate of soda remains in solution. It crystallizes in fine tetrahedrons, and is considerably more soluble than chlorate of potassa.

Phosphates of soda.—There are three crystallizable phosphates of soda belonging to the tribasic class, which I shall describe under their most usual names.

Phosphate of soda; $HO.2NaO.PO_5+24HO$; 359 *or* 4487.5.—This is the salt known in pharmacy as phosphate of soda, and formed by neutralizing phosphoric acid from burnt bones (page 319) with carbonate of soda. It crystallizes in oblique rhombic prisms, which are efflorescent, and essentially alkaline. M. Malaguti is, I believe, mistaken in ascribing 26 equivs. of water to this salt. The taste of phosphate of soda is cooling and saline, and less disagreeable than sulphate of magnesia, for which it may be substituted as an aperient. It dissolves in 4 times its weight of cold water, and fuses in its water of crystallization, when moderately heated. When evaporated above 90°, this salt crystallizes in another form with 14 instead of 24 atoms of water (Clark). It is deprived of half its alkali by hydrochloric acid in the cold, but not by acetic acid.

Subphosphate of soda; $3NaO.PO_5+24HO$; 381 *or* 4762.5.—Formed when an excess of caustic soda is added to the preceding salt. It crystallizes in slender six-sided prisms, with flat terminations, which are unalterable in air; but the solution of this salt rapidly absorbs carbonic acid, and is deprived of one-third of its alkali by the weakest acids. The crystals dissolve in 5 times their weight of water at 60°, and undergo the watery fusion at 170°. This salt continues tribasic after being exposed to a red heat.

Biphosphate of soda; $2HO.NaO.PO_5+2HO$; 139 *or* 1737.5.—Obtained by adding tribasic phosphate of water to phosphate of soda, till the latter ceases to produce a precipitate with chloride of barium. The solution affords crystals, in cold weather, of which the ordinary form is a right rhombic prism, having its larger angle of 93° 54′. But this salt is dimorphous, occurring in another right rhombic prism, of which the smaller angle is 78° 30′, terminated by pyramidal planes, isomorphous with binarseniate of soda. The biphosphate of soda is very soluble, and has a distinctly acid reaction. Like all the other soluble tribasic phosphates, it gives a yellow precipitate with nitrate of silver, which is tribasic phosphate of silver.

Phosphate of soda and ammonia, Microcosmic salt; $HO.NH_4O.NaO.PO_5+8HO$; 201 *or* 2512.5.—This salt is obtained by heating together 6 or 7 parts of crystallized phosphate of soda, and 2 parts of water, till the whole is liquid, and then adding 1 part of pulverized sal-ammoniac. Chloride of sodium separates, and the solution, filtered and concentrated, affords the phosphate in prismatic crystals. It is purified by a second crystallization. This salt occurs in urine. It is much employed as a flux in blow-pipe experiments. By a slight heat it loses 8HO, by a stronger heat it is deprived of its remaining water and ammonia, and converted into metaphosphate of soda, which is a very fusible salt. It will be observed that the three atoms of base in this phosphate are all different,—namely, water, oxide of ammonium, and soda; of which the two last belong to the same natural family, for bases of the same family may exist together in the salts of bibasic and tribasic acids, forming stable compounds, but not in ordinary double salts. No phosphate exists, corresponding with microcosmic salt, but containing potassa instead of oxide of ammonium; the phosphate of soda, with 14HO, has been mistaken for such a salt.

Pyrophosphate of soda; $2NaO.PO_5+10HO$; 134 + 90, *or* 1675 + 1125.—Procured by heating the phosphate of soda to redness, when it loses its basic water as well as its water of crystallization. The residual mass dissolved in water affords a salt, which is less soluble than the original phosphate, and crystallizes in prismatic crystals, which are permanent in air, and contain ten atoms of water. Its solution is essentially alkaline. This salt is precipitated white, by nitrate of silver. It is to be remarked that insoluble pyrophosphates, including pyrophosphate of silver, are soluble to a considerable degree in the solution of pyrophosphate of soda. The pyrophosphates of potassa and of ammonia can exist in solution, but pass into tribasic salts when they crystallize.

A *bipyrophosphate of soda* ($HO.NaO.PO_5$) exists, obtained by the application of a graduated heat to the biphosphate of soda, but it does not crystallize. Its solution has an acid reaction.

Metaphosphate of soda; $NaO.PO_5$, 103 *or* 1287.5.—The biphosphate of soda, containing only one equivalent of fixed base, affords the metaphosphate of soda, when heated to redness. The metaphosphate of soda fuses at a heat which does not exceed low redness, and on cooling rapidly forms a transparent glass, which is deliquescent in damp air, and very soluble in water, but insoluble in alcohol: its solution has a feebly acid reaction, which can be negatived by the addition of 4 per cent. of carbonate of soda. When evaporated, this solution does not give crystals, but dries into a transparent pellicle, like gum, which retains at the temperature of the air somewhat more than a single equivalent of water. Added to neutral, and not very dilute solutions of earthy and metallic salts, metaphosphate of soda throws down insoluble hydrated metaphosphates, of which the physical condition is remarkable. They are all soft solids, or semifluid bodies; the metaphosphate of lime having the degree of fluidity of Venice turpentine.

The bipyrophosphate of soda appears to undergo several changes under the influence of heat before it becomes metaphosphate. At a temperature of 500°, the salt becomes nearly anhydrous, and affords a solution which is *neutral* to test-paper, but in other respects resembles the bipyrophosphate. But at temperatures which are higher, but insufficient for fusion, the salt being anhydrous, appears to have lost its solubility in water; at least it is not affected at first when thrown in powder into boiling water, but gradually dissolves by continued digestion, and passes into the preceding variety.—(Phil. Trans. 1833, p. 275).

When the fused metaphosphate of soda is slowly cooled, it forms a crystalline mass, as observed by Fleitmann and Henneberg, and gives a crystallizable metaphosphate of soda (page 324).

Borax, Biborate of soda, $NaO.2BO_3+10HO$; $100.8+90$ *or* $1260.+1125.$—This salt is met with in commerce in large hard crystals. It is found in the water of certain lakes in Transylvania, Tartary, China, and Thibet, and is deposited in their beds by spontaneous evaporation. It is imported from India in a crude state, and enveloped in a fatty matter, under the name of *Tinkal,* and afterwards purified. But nearly the whole borax consumed in England is at present formed by neutralizing, with carbonate of soda, the acid from the boracic lagoons of Tuscany. The ordinary crystals of borax are prisms of the oblique system, containing 10 atoms of water, of density 1.692; but it also crystallizes at 133° in regular octohedrons, which contain only 5 atoms of water. This salt has a sweetish, alkaline taste; for, although containing an excess of acid, it has an alkaline reaction, like the bicarbonate of soda, and is soluble in 10 parts of cold, and 2 parts of boiling water.

The anhydrous salt is very fusible by heat, and forms a glass of density 2.367. This glass possesses the property of dissolving most metallic oxides, the smallest portions of which colour it. As the metal may often be discovered by the colour, borax is valuable as a flux in blow-pipe experiments. For this purpose a thin platinum wire is generally used, one end of which is bent into a hook (fig. 182.) The loop being slightly moistened, is dipped into a fine powder of anhydrous borax, and a minute portion of the metallic oxide which we wish to determine is also taken up on the loop. The matter is then fused in the flame of a candle or spirit-lamp directed upon it by means of a mouth blow-pipe (fig. 183.) Often

Fig. 182.

two different colourations are obtained when the metal has more than one oxide, according as the substance is heated in the reducing or white portion of the flame, which, in the blow-pipe flame, is at *b* (fig. 184), or in the oxidating spheres *a a*, and

FIG. 183.

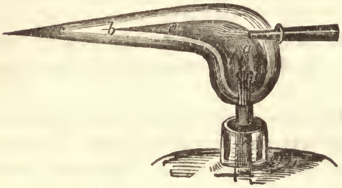
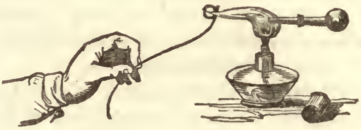


FIG. 184.



at the point *c*, where there is an excess of atmospheric air. To produce the colour of the protoxide, we expose to the reducing flame; and to produce the colour of the peroxide, we expose to the oxidizing flame.

As pieces of metal could not be soldered together if covered by oxide, borax is fused with the solder upon the surface of the metals to be joined, to remove the oxide. Borax is also a constituent of the soft glass, known as jewellers' paste, which is coloured to imitate precious stones. But the most considerable consumption of this salt is in the potteries, in the formation of a glaze for porcelain.

A neutral borate of soda is formed by calcining strongly 1 eq. of borax with 1 eq. of carbonate of soda, when carbonic acid is expelled. The solution yields a salt belonging to the oblique prismatic system, of which the formula is, $NaO.BO_3+8HO$. When heated, it fuses in its water of crystallization, and is expanded into a vesicular mass of extraordinary magnitude by the vaporization of that water.

When borax is fused with carbonate of soda in excess, the quantity of carbonic acid which escapes indicates the formation of a borate, $3NaO+2BO_3$, but which has not been farther examined. Notwithstanding this, a solution of borax in water is decomposed, and the boracic acid entirely liberated, by a stream of either carbonic or hydrosulphuric acid. Silicic acid, however, in its soluble modification, has no decomposing action upon a solution of borax. Boracic acid, therefore, appears to stand in the scale of acids above silicic, but below carbonic acid. A saturated solution of borax readily dissolves a large amount of arsenious acid, forming a compound remarkable for its great solubility in water. This contains, according to Prof. E. Schweizer, arsenite of soda, borate of soda, and a compound of arsenious and boracic acids, and is probably represented by the formula—

$$NaO.AsO_3+2(NaO.2BO_3)+2(BO_32AsO_3)+10HO.$$

A salt is said to exist, formed of $NaO+4BO_3$, but to crystallize with difficulty, produced on combining borax with a quantity of boracic acid equal to what it already contains. M. Laurent has also shown that a sexborate of soda exists in solution, but is not crystallizable. (Ann. de Ch. et de Phys. lxvii., 218.) The borates of potassa have also been examined by Laurent. The sexborate crystallizes well; its formula is $KO.6BO_3+10HO$. A triborate is represented by $KO.3BO_3+8HO$; the biborate corresponds in composition with octohedral borax, but has, notwithstanding, a different and incompatible form.

A simple and very accurate method of analyzing borax is, to add an excess of hydrochloric acid to a solution of the salt, and evaporate to dryness on the water-bath, adding a few more drops of hydrochloric acid towards the end of the operation. The mass, when perfectly dry, is re-dissolved in water, a little nitric acid mixed with the solution, and the chlorine precipitated by nitrate of silver; from the amount of chloride of silver that of the chlorine is deduced, and from the latter the quantity of soda. The alkaline bases of all the other borates may be obtained wholly as chloride by a similar treatment. (Schweitzer, Chem. Gaz. 1850, p. 281.)

Silicates of soda.—The earth silica, or silicic acid, SiO_3 (page 290), is dissolved by caustic soda, and gives, by slow evaporation, a crystallized silicate of soda, $3NaO.2SiO_3$ (Fritzsche). A concentrated solution of caustic soda at a high temperature under pressure dissolves silica freely even in the form of flint or of quartzy sand, and gives a similar silicate, which is used by Mr. Ransome of Ipswich for the induration of plaster and cements, and the formation of artificial stone.

When silicic acid is thrown into carbonate of potassa or soda, in a state of fusion by heat, a fusible silicate is formed, in which, judging from the quantity of carbonic acid expelled, 3 eq. of soda are also combined with 2 eq. of silicic acid, and the oxygen in the soda is to that in the silicic acid as 1 to 2. This silicate dissolves in the clear and liquid carbonate. When, on the other hand, a greater proportion of silicic acid is fused with the carbonate, the whole carbonic acid of the latter is expelled, and the excess of silicic acid then dissolves in the silicate. The silicic acid and silicate of such mixtures do not separate by crystallization, but uniformly solidify together, on cooling, as a homogeneous glass, whatever their proportions may be. It is thus impossible to obtain alkaline silicates, which are certainly definite combinations, in the dry way. A mixture of silicic acid with potassa or soda, in which the oxygen of the former is to that of the latter as 18 to 1, is said still to be fusible by the heat of a forge; but when the proportion is as 30 to 1, the mixture merely agglutinates, or frits. These combinations, even with a large quantity of silicic acid, continue to be soluble in water.

A compound, known as *soluble glass*, is obtained by fusing together 8 parts of carbonate of soda (or 10 of carbonate of potassa) with 15 of fine sand and 1 of charcoal. The object of the charcoal is to facilitate the combination of the silicic acid with the alkali, by destroying the carbonic acid, which it converts into carbonic oxide. This glass, when reduced to powder, is not attacked by cold water, but is dissolved by 4 or 5 parts of boiling water. The solution may be applied to objects of wood, and, when dried by a gentle heat, forms a varnish, which imbibes a little moisture from the air, but is not decomposed by carbonic acid, nor otherwise alterable by exposure. Stuffs impregnated with the solution lose much of their combustibility, and wood is also defended by it, to a certain degree, from combustion.

GLASS.

The alkaline silicates, cooled quickly or slowly, never exhibit a crystalline structure, but are uniformly vitreous (p. 151). They are the bases of the ordinary varieties of glass, which contain earthy silicates besides, but appear to owe the vitreous character to the silicates of potassa and soda. The silicate of lime, and the silicate of the protoxide of iron, crystallize on cooling; so does the silicate of lead, unless it contains a large excess of oxide of lead. The addition of the silicate of potassa or soda deprives them entirely of this property; the silicate of alumina considerably diminishes it. But if silicates of potassa or soda are heated for a long time, the alkali may in part escape in vapour, and if other bases exist in the compound, it then often assumes a crystalline structure on cooling. The alkaline silicates by themselves are soluble in water, and decomposed by acids; the silicate of lime is also dissolved by acids, but the double silicates, on the contrary, resist the action of acids, particularly when they contain an excess of silicic acid, and form an available glass. The following table exhibits the composition of the best known kinds of glass, from the analyses of Dumas and of Faraday:—

COMPOSITION OF VARIETIES OF GLASS.

	Silicic acid.	Potassa.	Lime.	Ox. lead.	Alumina.	Water.
Bohemian glass	69	12	9	0	10	0
Crown-glass	63	22	12	0	3	0
Window-glass	69	11 soda	13	0	7	0
Bottle-glass	54	5	29	6 ox. iron	0	0
Flint-glass	45	12	0	43	0	0
Crystal	61	6	0	33	0	0
Strass	38	8	0	53	1	0
Soluble glass	62	26	0	0	0	12

The analysis, by Mr. T. Rowney, of the superior Bohemian glass, which, on account of its difficult fusibility, is employed for combustion-tubes, gave silicic acid 73.13, potassa 11.49, soda 3.07, lime 10.43, alumina 0.30, sesquioxide of iron 0.13, magnesia 0.26, protoxide of manganese 0.46=99.27. The oxygen of the bases is to that of the silicic acid as 1 to 6. The specimen was decomposed by fusion with carbonate of soda, for the earths, and by fusion with hydrate of baryta for the alkalies (Mem. Chem. Soc. iii. 299).

Silicate of soda and lime. — To form window-glass, 100 parts of quartzy sand are taken, with 35 to 40 parts of chalk, 30 to 35 parts of carbonate of soda, and 180 parts of broken glass. These materials are first fritted, or heated so as to cause the expulsion of water and carbonic acid, and to produce an agglutination of their particles, and afterwards completely fused in a large clay crucible of a peculiar construction; or fused at once, the fritting being now generally discontinued. For the first formation of the glass a higher temperature is required than that at which it is most thick and viscid, and in the proper condition for working it. At the latter temperature the substance possesses an extraordinary degree of ductility, and may be drawn out into threads so fine as to be scarcely visible to the eye. A portion of the plastic mass, on the extremity of an iron tube used as a blow-pipe, may be expanded into a globular flask, and pressed or bent into vessels of any form, which may be pared and fashioned by the scissors. At a lower temperature, glass vessels become rigid, and, when cold, brittle in the extreme, unless they be *annealed*, that is, kept for several hours at a temperature progressively lowered from the highest degree which the glass can bear without softening to the temperature of the atmosphere. The well-known glass tears, or Prince Rupert's drops, as they are called, which are made by allowing drops of melted glass to fall into water, illustrate the peculiar properties of unannealed glass. The surface becoming solid by the sudden cooling, while the interior is still at a high temperature, and consequently dilated, the drop is of greater volume than it would be if cooled slowly and equally throughout its mass. Its particles are thus in a state of extreme tension, and an injury to any part causes the whole mass to fly to pieces. The fracture of unannealed vessels, which is the immediate consequence of scratching their surface, has been compared to the effect upon a sheet of cloth forcibly stretched, of injuring its edge in the smallest degree by a knife or scissors. It then ceases to preserve its integrity by resisting the tension, and is torn across. The relative proportions of the ingredients of this and other species of glass is subject to some variation. But the oxygen in the bases of window-glass is to the oxygen of the silicic acid nearly as 1 to 4; the composition approaching the formula $3NaO.3CaO+8SiO_3$. This glass has a green tint, which is very obvious in a considerable mass of it, occasioned in part, it may be, by the impurities of the materials, but a certain degree of which appears to be essential to a soda-glass. For in all the finer and entirely colourless varieties of glass it is necessary to use potassa.

Silicates of potassa and lime. — Plate-glass used for mirrors, crown-glass, and the beautiful Bohemian glass, are of this composition. In the most remarkable varieties the oxygen of the bases is to that of the acid as 1 to 6, and the oxygen of the lime to that of the potassa in proportions which vary from 1 and $\frac{2}{3}$ to 1 and 1. Its composition approaches the formula $KO.CaO + 4SiO_3$. This is the glass of most difficult fusibility, and therefore most suitable for the combustion-tubes employed in organic analysis. From its purity, and the absence of oxide of lead, it is also made the basis of most coloured glasses, and of stained glass. To produce coloured glasses certain metallic oxides are mixed with the fused glass in the pot; oxide of cobalt, for instance, for a blue colour, oxide of copper for green, binoxide of manganese in small proportion for an amethystine glass, and in large proportion for a black glass, peroxide of uranium for a delicate lemon-yellow tint, and gold for a ruby glass. In stained glass, on the other hand, the metal or metallic oxide is merely applied with a proper flux to the surface of the glass, which is then exposed in an oven to a temperature sufficient to fuse the colouring matter, without distorting the sheet of glass. Different shades of yellow and orange are thus produced by means of silver and antimony, and a superb ruby-red by a proper, but difficult, application of suboxide of copper. The beautiful avanturine glass contains crystals of metallic copper. The green shade of ordinary glass is chiefly due to protoxide of iron, and is corrected by a small addition of binoxide of manganese (hence called *pyrolusite*), which raises the iron to the state of sesquioxide, in which it is not injurious, while, at the same time, the binoxide of manganese, by losing oxygen, passes into the state of the colourless protoxide of that metal.

Silicates of potassa and lead.—These substances enter into the composition of the purer and more brilliant species of glass in use in this country; such as that called crystal, of which most drinking vessels are made, flint-glass for optical purposes, and strass, which is employed in imitations of the precious stones. For crystal, the materials are taken in the following proportions: 120 parts of fine sand, about 40 of purified potashes, 35 of litharge or minium, and 12 of nitre. In this glass the oxygen of the bases is to that of the silicic acid as 1 to a number which may vary from 7 to 9, and the oxygen of the potassa is to that of the oxide of lead as 1 to a number varying from 1 to 2.5. In flint-glass, and in strass, the oxygen of the bases is to that of the silicic acid as 1 to 4, and the oxygen of the potassa is to that of the oxide of lead as 2 to 3 in flint-glass, and as 1 to 3 in strass (Dumas). The more oxide of lead glass contains, the higher its density; the density of this kind of glass exceeding 3.6, while that of the Bohemian glass does not rise higher than 2.4. Glass containing oxide of lead is recommended by its greater fusibility and softness, by which it is more easily fashioned into various forms, and by its great brilliancy, which is remarkable in lustres and other objects of cut glass. The presence of lead in glass is at once discovered by its surface acquiring a metallic lustre when heated to redness in the reducing flame. ***Enamel*** is a white and very fusible glass, containing a white opaque substance suspended in its mass. It is generally prepared from the stannate of lead, formed by heating and oxidizing together 15 parts of tin and 100 of lead. This is afterwards fused with 50 parts of sand and 40 parts of carbonate of potassa. Besides binoxide of tin, arsenious acid, oxide of antimony, phosphate of lime, and sulphate of potassa, are employed to give opacity to enamel.

Silicates of alumina, of the oxides of iron, magnesia, and potassa or soda.—Green or bottle-glass, of which wine-bottles, carboys, and glass articles of low price consist, is a mixture of these silicates. It is formed of the cheapest materials, such as sand, with soap-makers' waste, lime that has been used to render alkali caustic, &c. In the bottle-glass of this country the small quantity of alkali is chiefly soda. The alkaline sulphates, when fused with silicic and carbonaceous matter, lose their sulphuric acid, and become silicates; even common salt is decomposed by the united action of silicic acid and the aqueous vapour in flame, but much of it is lost from its own volatility. The proportion of silicic acid to the bases is much less in this than in the other kinds of glass, the oxygen of the former being to the latter as 2 to 1; and the oxygen of the alumina and sesquioxide of iron equal to that of the potassa and lime. This glass is, in fact, a mixture of neutral and subsilicates, and, when it contains an excess of lime, is more apt than any of the preceding species to assume a crystalline structure when maintained long in a soft condition by heat.

A bottle of green glass may be devitrified, or converted into what is called Reaumur's porcelain, by enveloping it in sand, and placing it where its temperature is kept high for several weeks, as in a brick-kiln or porcelain-furnace. Glass of all kinds, when strongly and repeatedly heated, loses alkali, from its volatility; the glass then becomes harder and less fusible, and is not so easily wrought,—a circumstance which may sometimes be remarked in blowing a bulb upon a tube which has been too long exposed to the blow-pipe flame. Glass of all kinds, when well manufactured, is supposed to be insoluble in water, but it is eventually acted upon, and soonest when its natural surface is broken; water tending to resolve glass into a soluble alkaline silicate and an insoluble earthy silicate. Glass bottles containing a large proportion of lime may be corroded through by sulphuric acid. An excess of alumina also makes glass very easily attacked by acids, even by the bitartrate of potassa in wines. In common with all natural and artificial silicates, glass is attacked by hydrofluoric acid, with the formation of the volatile fluoride of silicon. (See the Treatise on Glass, in Knapp's Chemical Technology, edited by Ronalds and Richardson, vol. ii.)

Ultramarine.—This beautiful blue pigment is extracted by mechanical operations from the mineral *Lapis lazuli.* The structure of the mineral is granular and slightly laminated: its constituents are, silicic acid 45.40, alumina 31.67, soda 9.09, sulphuric acid 5.89, sulphur 0.95, lime 3.52, iron 0.86, chlorine 0.42, water 0.12=97.92. It was first imitated successfully by M. Guimet in 1827. The process, according to M. Debette, appears to be first the preparation of a polysulphide of sodium, which is afterwards calcined with prepared clay and protosulphate of iron, so as to form sulphide of iron. The last product in fine powder is heated in a muffle with exposure to air for several hours, when it becomes in succession brown, red, green, and blue. The excess of sulphide of sodium and other salts is washed out of the powder, which, dried and washed again at a moderate temperature, gives an ultramarine of a magnificent blue tint. The process is an extremely delicate one, and the nature of the substance which gives the blue colour is very obscure. A sulphide of sodium is supposed to be essential to its composition, as the colour is destroyed by acids, with evolution of the hydrosulphuric acid; while the substitution of carbonate of potassa for carbonate of soda gives a compound corresponding to ultramarine, but which is colourless. (Pelouze et Fremy, Cours de Chim. Génér. ii. 117).

SECTION III.

LITHIUM.

Eq. 6.43 *or* 80.37; Li.

Lithium is the metallic basis of a rare alkaline oxide, lithia, discovered in 1818 by Arfwedson. (Ann. de Ch. et de Ph. x. 82). The name lithia (from λίθειος, stony) was applied to it, from its having been first derived from an earthy mineral. The metal was obtained by Davy by the voltaic decomposition of lithia, and observed to be white, resembling sodium, and to be highly oxidable. The equivalent of lithium is much smaller than that of any other metal, and its oxide has therefore a high saturating power.

Lithia; LiO.—The only known oxide of lithium is a protoxide. It exists in small quantities in the minerals spodumene or triphane, petalite, and lepidolite; but the mineral containing lithia, which is most abundant, is a native phosphate occurring at Rabenstein in Bavaria, and which consists of phosphoric acid 42.64, oxide of iron 49.16, oxide of manganese 4.75, and lithia 3.45. This mineral is dissolved in hydrochloric acid, the iron peroxidized by a little nitric acid, the solution diluted with water, and then ammonia added, which precipitates the insoluble phosphate of sesquioxide of iron. The manganese is afterwards removed by hydrosulphuric acid, the liquid filtered, evaporated to dryness, and the residue calcined to volatilize the ammoniacal salts; the chloride of lithium is then taken up by alcohol.

The hydrate of lithia resembles hydrate of potassa in causticity, but is less soluble in water, and loses its combined water at an elevated temperature. Sulphur acts upon it in the same manner as upon potassa. Its salts are colourless.

The chloride is very soluble in water, as well as in absolute alcohol, and fuses at a high temperature. It crystallizes in cubes containing 4HO.

The carbonate of lithia has a certain degree of solubility, and its solution has an alkaline reaction, properties upon which the claim of lithia to be ranked among the alkalies, instead of the alkaline earths, is chiefly rested. The fluoride of lithium has the sparing solubility of the carbonate.

The sulphate of lithia is soluble, and presents itself in fine crystals, which are persistent in air. It forms a double salt with sulphate of soda, of which the formula is $LiO.SO_3 + NaO.SO_3 + 6HO$. The nitrate and acetate are both very soluble and deliquescent.

The neutral phosphate of lithia is slightly soluble in water, but considerably more so than the double phosphate of lithia and soda, which remains as an insoluble powder when the solution of lithia is evaporated to dryness with that of phosphate of soda. Hence phosphate of soda is used as a test of lithia. The salts of lithia are also recognized, when heated on platinum wire before the blow-pipe, by tinging the flame of a red colour.

[*See Supplement*, p. 811.]

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION I.

BARIUM.

Eq. 68.64 *or* 858; Ba.

Barium, the metallic basis of the earth baryta, was obtained by Davy in 1808, by the voltaic decomposition of moistened carbonate of baryta in contact with mercury: it may likewise be procured by passing potassium in vapour over baryta heated to redness in an iron tube, and afterwards withdrawing the reduced barium, which the residue contains, by means of mercury. The latter metal is separated by distillation in a glass retort, care being taken not to raise the temperature to redness, for the barium then decomposes glass. Barium is a white metal like silver, fusible under a red heat, denser than oil of vitriol, in which it sinks. It oxidates with vivacity in water, disengages hydrogen, and is converted into baryta. It is named barium (from βαρύς, heavy), in allusion to the great density of its compounds.

Baryta; BaO, 76.64 *or* 958.—This earth exists in several minerals, of which the most abundant are sulphate of baryta or heavy-spar, and the carbonate of baryta or witherite. The earth is obtained in the anhydrous condition and pure, by calcinating nitrate of baryta, at a bright-red heat, in a porcelain retort, or in a well-covered crucible of porcelain or silver, but not of platinum. Baryta is a grey powder, of which the density is about 4. When heated to redness in a porcelain tube, and oxygen gas passed over it, it absorbs that gas with avidity, and becomes binoxide of barium, the compound for the preparation of which anhydrous baryta is chiefly required. Baryta slakes and falls to powder when water is thrown upon it, combining with one equivalent of water with the evolution of so much heat as to become incandescent.

Hydrate of baryta is a valuable reagent. Of the different processes for this substance, one of the most convenient is that from the native sulphate. This is a soft mineral, and easily reduced to an impalpable powder, which is intimately mixed with one-eighth of its weight of coal pounded and sifted, or with one-third charcoal-powder and one-fourth resin; the mixture is introduced into a Cornish crucible, and exposed in a furnace to a bright-red heat for an hour. The sulphate is converted by this treatment into sulphide of barium; the last salt is dissolved out of the black residuary mass by boiling water, and the solution, which generally has a yellow tint but is sometimes colourless, is filtered while still hot. The solution, if strong, may crystallize on cooling, in thin plates. As the sulphide absorbs oxygen from the air, and returns to the state of sulphate of baryta, it must not be exposed long in open vessels. To a boiling solution of sulphide of barium in a flask, black oxide of copper from the nitrate is added, in successive small portions, till a drop of the liquid ceases to blacken a solution of lead, and precipitates it entirely white: the liquid then contains only hydrate of baryta in solution. It may immediately be filtered, with little access of air, to prevent absorption of carbonic acid. The decomposition in this process, for which we are indebted to Dr. Mohr of Coblentz, is rather complicated. Six eq. of sulphide of barium and 8 eq. of oxide of copper producing 5 eq. of baryta, 1 eq. of hyposulphite of baryta, and 4 eq. of subsulphide of copper, of which the first only is soluble:

$$6\ \mathrm{BaS}\ \text{and}\ 8\mathrm{CuO} = 5\mathrm{BaO}\ \text{and}\ \mathrm{BaO.S_2O_2}\ \text{and}\ 4\mathrm{Cu_2S}.$$

Binoxide of manganese may be substituted in this process for oxide of copper, but generally gives a solution of baryta coloured by some impurity. The reaction is then similar:

$$6\mathrm{BaS}\ \text{and}\ 4\mathrm{MnO_2} = 5\mathrm{BaO}\ \text{and}\ \mathrm{BaO.S_2O_2}\ \text{and}\ 4\mathrm{MnS}.$$

If the solution of sulphide of barium has been concentrated, the greater part of the hydrate of baryta separates on cooling in voluminous and transparent crystals, containing 10HO.

Hydrate of baryta may also be obtained by adding caustic potassa to a saturated solution of chloride of barium; hydrate of baryta precipitates, and must be redissolved in boiling water, and crystallized by cooling, to purify it. It is soluble in 3 parts of boiling water, and in 20 parts of water at 60°. Baryta retains 1 eq. of water with great force like the fixed alkalies. This combination is fusible a little below redness, and runs like an oil; it congeals into a crystalline mass, which attracts carbonic acid very slowly from air, and is therefore the most favourable position in which to preserve hydrate of baryta.

The solution of baryta is strongly caustic, although less so than potassa or soda, and disorganizes organic matter rapidly; it is poisonous, in common with all the soluble preparations of barium. Chlorine decomposes baryta in the same manner as it does the alkalies. Sulphur is dissolved in the solution of baryta with the aid of heat, and, according to the temperature, a sulphate or hyposulphite is formed, with the trisulphide of barium of a green colour. When heated to redness in the vapour of phosphorus, baryta is converted into phosphate of baryta and phosphide of barium. On dropping oil of vitriol upon dry baryta and strontia, the combination is said to produce light with the first, but not with the second. Baryta, whether free or in combination with an acid as a soluble salt, is discovered by means of sulphuric acid, which throws down sulphate of baryta, a compound not decomposed by, nor soluble in, nitric and hydrochloric acids.

Binoxide of barium; $\mathrm{BaO_2}$; 84.64 *or* 1058.—This compound is prepared by exposing anhydrous baryta, from the nitrate, to pure oxygen at a red heat; or by heating pure baryta to low redness in a porcelain-crucible, and then gradually adding chlorate of potassa, in the proportion of about 1 part of the latter to 4 of the former.

The chloride of potassium formed at the same time, is removed, by cold water, from the binoxide of barium, while the latter unites with 6HO. Binoxide of barium, when decomposed by dilute acids with proper precautions, affords binoxide of hydrogen.

Chloride of barium; BaCl+2HO; 104.14+18 *or* 1301.76+225.—A reagent of constant use, which is obtained by dissolving native carbonate of baryta in pure hydrochloric acid diluted with 3 or 4 times its bulk of water, or by neutralizing sulphide of barium by the same acid. It crystallizes from a concentrated solution in flat four-sided tables, bevelled at the edges. The crystals contain 2HO (14.75 per cent. of water), which they lose below 212°. They are said to be soluble in 400 parts of anhydrous alcohol: 100 parts of water dissolve 43.5 parts at 60°, and 78 parts at 222°, which is the boiling-point of the solution.

Carbonate of baryta; $BaO.CO_2$; 98.64 *or* 1233.01.—This salt consists in 100 parts of 22.41 carbonic acid, and 77.59 baryta. The density of the native carbonate is 4.331; it is not attacked by sulphuric acid, and retains its carbonic acid at the highest temperatures. The precipitated carbonate is decomposed by sulphuric acid, and loses its carbonic acid when calcined at a white heat, in contact with carbonaceous matter. It is obtained of greater purity when precipitated by the carbonate of ammonia, than by the carbonate of potassa or soda, portions of which are apt to go down in combination with carbonate of baryta. Although reputed an insoluble salt, carbonate of baryta is soluble in 2300 parts of boiling water, and in 4300 parts of cold water. It is still more soluble in water containing carbonic acid, and is highly poisonous. The precipitated carbonate of baryta, or, better, the hydrate of baryta, is employed in the analysis of silicious minerals, containing an alkali, which are not soluble in an acid. The mineral, in the state of an impalpable powder, is intimately mixed with 4 or 5 times its weight of the hydrate, and exposed in a silver-crucible to a red heat, which occasions a semi-fusion of the mixture and the decomposition of the silicates; the mineral afterwards dissolving entirely in an acid, with the exception of its silica.

Sulphate of baryta; $BaO.SO_3$; 116.64 *or* 1458.01.—This salt consists, in 100 parts, of 34.37 sulphuric acid and 65.63 baryta. The density of heavy-spar, or the native sulphate, varies from 4 to 4.47. It occurs in considerable quantities in trap and other igneous rocks, forming often veins of several feet in thickness, and miles in extent. It is mined for the purpose of being substituted for carbonate of lead, or being mixed with that substance, when used as a pigment. When chloride of barium is added to sulphuric acid, or to a soluble sulphate, at the boiling temperature, sulphate of baryta precipitates readily, in a dense crystalline powder, which may easily be collected and washed on a filter. It is completely insoluble in water and dilute acids, but is soluble in concentrated and boiling sulphuric acid, from which it crystallizes on cooling. Precipitated sulphate of baryta is partially decomposed in a concentrated and boiling solution of carbonate of potassa or soda, and carbonate of baryta formed.

Nitrate of baryta; $BaO.NO_5$; 130.64 *or* 1633.01.—This salt crystallizes in fine transparent octohedrons, which are anhydrous. It is obtained by dissolving carbonate of baryta in nitric acid diluted with 8 or 10 times its weight of water; or by mixing the acid, also in a diluted state, with the solution of sulphide of barium. It requires 12 parts of water at 60°, and 3 or 4 parts of boiling water, for solution; it is insoluble in alcohol. The nitrate of baryta is employed as a reagent, and also in procuring anhydrous baryta.

The chlorate and hyposulphate of baryta are soluble, the iodate, sulphite, hyposulphite and phosphates of baryta, insoluble salts.

[*See Supplement*, p. 812.]

SECTION II.

STRONTIUM.

Eq. 43.84 *or* 548.02. Sr.

Strontium is prepared in the same way as barium, which it greatly resembles. It is a white metal, denser than oil of vitriol. It derives its name from Strontian, a mining village in Argyleshire.

Strontia, Strontian, or *Strontites;* SrO; 51.84 *or* 648.02. — The native carbonate of strontia was first distinguished from carbonate of baryta by Dr. Crawford, in 1790, who conceived the idea that the former mineral might contain a new earth. This conjecture was verified in 1793, by Dr. Hope (Edinb. Trans. iv. 14); and much about the same time also by Klaproth. The earth, strontia, is to baryta what soda is to potassa. It occurs in nature as carbonate and more abundantly as sulphate. Strontia may be prepared by a strong calcination of the native carbonate in contact with carbon. It is lighter than baryta, and has a taste which is less acrid and caustic, but stronger than that of lime. It is said not to be poisonous. The hydrate crystallizes with 9HO, but retains only one equivalent at 212° (Mr. Smith). This last hydrate enters into fusion at a very high temperature, without losing its combined water. The anhydrous earth, like baryta, is infusible. The crystallized hydrate requires 52 parts of water to dissolve it at 60°, but only twice its weight at 212°.

The soluble salts of strontia are prepared from the carbonate. They are precipitated by sulphuric acid and by soluble sulphates, but not so completely as the salts of baryta, the sulphate of strontia having a small degree of solubility. Hence, when sulphate of soda is added in excess to a salt of strontia, and the precipitate separated by filtration, so much sulphate of strontia remains in solution, that the liquid yields a white precipitate with carbonate of soda (Dr. Turner). Most of the salts of strontia, when heated on platinum-wire before the blow-pipe, communicate a red colour to the flame. Baryta and strontia in solution may be separated by hydrofluosilicic acid, which precipitates baryta, but forms with strontia a salt very soluble in a slight excess of acid. Hyposulphite of strontia being soluble, while hyposulphite of baryta is insoluble, these earths may also be distinguished by means of hyposulphite of soda.

Binoxide of strontium, obtained by Thénard in brilliant crystalline scales, on adding binoxide of hydrogen to a solution of strontia. It contains two eq. of oxygen.

Chloride of strontium crystallizes in slender prisms, which contain 9HO, and are slightly deliquescent. This salt is soluble in three-fourths of its weight of cold water, and in all proportions in boiling water. At the ordinary temperature it dissolves in 24 parts of anhydrous alcohol, and in 19 parts of alcohol boiling. In this respect it differs from chloride of barium, which is insoluble in alcohol. Chloride of strontium communicates to flame a fine red tint. In the anhydrous condition this chloride absorbs 4 eq. of ammonia, and becomes a white bulky powder.

Carbonate of strontia forms the mineral *strontianite,* which generally has a fibrous texture, and is sometimes transparent and colourless, but generally has a tinge of yellow or green. Its density varies from 3.4 to 3.726. This salt is said to be soluble in 1536 parts of boiling water. It is more soluble in water containing carbonic acid, and occurs in some mineral waters. It retains its carbonic acid when calcined.

Sulphate of strontia is known as *celestine,* and occurs in regular crystals of the same form as sulphate of baryta. Its density is about 3.89. It is soluble in from 3000 to 4000 parts of water, and the solution is sensibly precipitated by chloride of barium. The mineral is found in considerable quantity associated with volcanic sulphur, and in other formations. A large deposit of it exits in the neighbourhood of Bristol, from which it may be obtained in sufficient quantity for any application in the arts. The various compounds of strontium may be prepared from the sulphate of strontia precisely in the same manner as those of barium from the sulphate of baryta.

Hyposulphite of strontia is crystallizable, and soluble in 4 parts of cold, and 1¾ parts of boiling water. It loses 31 per cent. of water of crystallization between 122° and 140°, without any other change.

Nitrate of strontia crystallizes at a high temperature in regular octohedrons, of density 2.857, which are anhydrous, but it is generally obtained at a low temperature in crystals, which contain 5HO, of density 2.113 (Filhol). The anhydrous salt dissolves in 5 parts of cold water, and in 1 part of boiling water. A deflagrating mixture, which produces an intensely red illumination, is formed of 40 parts of nitrate of strontia, 13 parts of flowers of sulphur, 5 parts of chlorate of potassa, and 4 parts of sulphide of antimony.

The salts of baryta, strontia, and protoxide of lead, are strictly isomorphous, and greatly resemble each other in solubility and other properties. Hydrofluosilicic acid is employed to separate baryta from strontia, as it precipitates the former but not the latter. Neutral chromate of potassa, which precipitates salts of baryta immediately, precipitates only slowly the salts of strontia. In analysis, strontia is generally estimated as sulphate, but as the latter is not completely insoluble, an addition of alcohol is made to the water employed to wash the precipitate.

[*See Supplement*, p. 814.]

SECTION III.

CALCIUM.

Eq. 20, *or* 250; Ca.

Davy obtained evidence of the existence of this metal, and of its analogy to the preceding metals. It is the basis of lime. The name applied to it is derived from calx. [*See Supplement*, p. 815.]

Lime; CaO; 28, *or* 350.—Uncombined lime, or quicklime, as it is termed in the arts, is obtained by heating masses of limestone (carbonate of lime) to redness in an open fire, or lime-kiln. The escape of the carbonic acid is favoured by the presence of aqueous vapour and the gases of the fire, into which that gas can diffuse (page 181). In a covered crucible, carbonate of lime may be fused by heat without decomposition. The lime, properly burnt, remains in porous masses, which may be easily separated from the ashes of the fuel, and are sufficiently hard to be transported from place to place without falling to pieces. Although these masses appear light, the density of lime is not less than 2.3, or even 3.08, according to Royer and Dumas. Water thrown upon them, is first imbibed, and afterwards combines with the lime, which falls to powder in the state of hydrate, and is then said to be slaked. In this combination the temperature may rise to 572°, (300° C.), or sufficiently high to char wood. From its affinity for water, quicklime is applied to deprive certain liquids, such as alcohol, of the water they contain. To obtain pure lime, the crystallized carbonate should be calcined, such as calcareous spar, or Carrara marble. Lime, in common with other infusible earths, phosphoresces strongly when heated to full redness.

The only hydrate of lime known contains 1 eq. of water, which it loses at a lowred heat. It is sparingly soluble in water, but more soluble in cold than in hot water. According to Dalton, lime-water formed at 60°, 130°, and 212°, contains 1 grain of lime in 778, 972, and 1270 grains of water. Hence water saturated in the cold deposits hydrate of lime when boiled. By evaporating the solution in vacuo, Gay-Lussac obtained the same hydrate of lime in small transparent crystals of the hexahedral form. The *milk* or *cream* of lime is merely the hydrate diffused through water. In preparing lime-water, 3 or 4 ounces of slaked lime are agitated several times, during two or three hours, with two quarts of distilled water, and then allowed to settle. The lime-water first drawn off generally contains a little potassa, and should not therefore be considered pure. Lime-water has a harsh acrid taste, is alkaline, and, to a certain extent, caustic. It precipitates carbonic, silicic, boracic, and phosphoric acids from solutions of their alkaline salts. It dissolves oxide of lead. Lime-water absorbs carbonic acid rapidly from the air, and becomes covered by a pellicle of carbonate of lime. Hydrate of lime has the same property, absorbing about half an equivalent of carbonic acid with avidity, but not acquiring quite so much as three-fourths of an equivalent by two or three weeks' exposure to an atmosphere of the gas. Fuchs observed, that when hydrate of lime is exposed to air, it absorbs only half an equivalent of carbonic acid, and that a definite compound of hydrate and carbonate was formed. In the anhydrous condition, lime exhibits no affinity for carbonic acid.

Lime is characterized by affording a bulky precipitate of sulphate of lime, when sulphuric acid is added to its soluble salts. But as the sulphate of lime has a certain degree of solubility, this precipitate does not appear in very dilute solutions of these salts, nor in lime-water, a property by which lime may be distinguished from baryta and strontia. Sulphate of lime may also, when precipitated, be re-dissolved by the addition of nitric acid. Lime is entirely precipitated from neutral solutions by oxalate of ammonia, the oxalate of lime being completely insoluble. In the quantitative estimation of this earth, it is therefore generally thrown down as oxalate, and afterwards obtained as carbonate of lime, by heating the oxalate nearly to redness in a platinum crucible, in which a small fragment of carbonate of ammonia is dissipated at the same time, to prevent any lime becoming caustic by loss of carbonic acid.

Lime is applied to a variety of useful purposes in ordinary life and in the arts, of which the most important are its applications as a manure for land, and as mortar. In the first application, lime appears to be chiefly useful, (1) in promoting the oxidation and decomposition of the insoluble organic matters which the soil contains, and thereby rendering them capable of sustaining vegetable life; (2) in decomposing clay and rendering its potassa soluble, and (3) in restoring to the soil the calcareous element which is annually removed in the crop. In the formation of mortar, the hydrate of lime is mixed with 2 parts of coarse, or 3 parts of fine sand, and made into a paste with water. In building, a stone is laid upon a bed of this paste, which it compresses by its weight, imbibing moisture also from the mortar, which escapes principally through the porous stone. On drying, the mortar binds the stones between which it is interposed, and its own particles cohere so as to form a hard mass, solely by the attraction of aggregation, for no chemical combination takes place between the lime and sand, and the stones are simply united as two pieces of wood are by glue. The sand is useful in rendering insignificant by its mass the contraction of the mortar on drying, and also, from the large size of its grains, in rendering the dry mortar less short and friable. The mortar is subject to an ulterior change, from the slow absorption of carbonic acid, but even in the oldest mortar the conversion of the hydrate of lime into carbonate is never complete. The lime which is called *fat* slakes easily, and with considerable increase of volume; *lean* or poor lime slakes imperfectly, owing frequently to the presence of magnesia in a proportion exceeding 10 or 12 per cent; the latter earth having a comparatively feeble affinity for water. Magnesian lime is also generally considered prejudicial in agriculture, owing, it is supposed, to the magnesia long remaining caustic in the soil.

Some limestones, containing about 20 per cent of clay or silicate of alumina, afford lime which possesses a valuable property, that of forming with water a mass which becomes solid in a few minutes, and therefore hardens in structures covered by water. An excellent hydraulic mortar of this kind is obtained from concretionary masses found in marl, and also as isolated blocks in the bed of the Thames. This lime being burnt, ground, and sifted, when mixed with water to form a paste, sets as quickly as Paris plaster; its solidity increases with the time it has been submerged, and it ends by acquiring the hardness of limestone. Sand is added to it when it is used as common mortar, or in covering buildings to imitate stone. From the minute division of the silicic acid and alumina in this mortar, their combination with lime is more likely to occur than in ordinary mortar. Still the first setting of hydraulic mortar seems to be due simply to the fixation of water, and formation of a solid hydrate like gypsum. Hydraulic mortar is sometimes made by mixing together clay and chalk, and calcining the mixture, or more frequently by adding to hydrate of lime puzzolano ground to fine powder. The latter is a silicious substance of volcanic origin, composed principally of pumice, of which a stratum is excavated in the neighbourhood of Naples. The mortar which it makes with lime has obtained the name of Roman cement.

The hydrate of *binoxide of calcium* precipitates on adding lime-water, drop by drop, to a solution of binoxide of hydrogen. It contains, according to Thénard, 2 eq. of oxygen.

The *protosulphide of calcium* is procured by decomposing sulphate of lime, at a red heat, by hydrogen or charcoal. When newly prepared, it phosphoresces in the dark. It is only very sparingly soluble in water, but it is decomposed by boiling water, according to M. H. Rose, into hydrosulphate of sulphide of calcium, which is soluble, and hydrate of lime. Sulphide of calcium, when moistened with water, is readily decomposed by a stream of carbonic-acid gas, with the evolution of hydrosulphuric acid:

$$CaS.HO \text{ and } CO_2 = CaO.CO_2 + HS.$$

When hydrate of lime is boiled with sulphur and water, and the liquor allowed to cool before it is completely saturated with sulphur, yellow crystals separate from it, which are a *bisulphide of calcium*, combined with 3HO, according to the observations of Herschel. When lime, or protosulphide of calcium, is boiled with excess of sulphur, it dissolves sulphur till a *pentasulphide of calcium* is formed, which resembles in properties the corresponding degree of sulphuration of potassium.

Phosphide of calcium.—Small fragments of quicklime being heated to redness by a spirit-lamp, in a small mattrass with a long neck, and fragments of phosphorus dropped into the same vessel, a mixture is obtained of phosphate of lime and phosphide of calcium. The compound has a chocolate-brown colour. When the temperature is raised too high, the affinities change, and phosphorus escaping in vapour, nothing but lime remains. According to M. P. Thénard, in the reaction which gives phosphide of calcium, 7 eq. of phosphorus act upon 14 eq. of lime:

$$14CaO \text{ and } 7P = 2(2CaO.PO_5) \text{ and } 5Ca_2P.$$

The phosphide, therefore, contains 2 eq. of calcium to 1 eq. of phosphorus, and is analogous to the liquid hydride of phosphorus PH_2. When thrown into water, it is immediately transformed into the hydride of phosphorus referred to, which is spontaneously inflammable, and hypophosphite of lime, which is dissolved.

Chloride of calcium; CaCl; 55.50 *or* 693.75.—Obtained by neutralizing hydrochloric acid with carbonate of lime, or as a residue in several processes; a concentrated solution affords crystals in large striated four-sided prisms, which contain 6 eq. of water. Dried with stirring, above 212°, it affords a crystalline powder, containing 2 eq. of water, which produces an intense degree of cold when mixed with snow (p. 62). The same hydrate was produced on drying the crystals in vacuo over sulphuric acid for ten days. The crystals are soluble in one-fifteenth of their weight of water at 60°, and exceedingly deliquescent. The salt is made anhydrous by heat, and undergoes the igneous fusion at a red heat. The liquid chloride is poured upon a slab, and the transparent cake of solid salt immediately broken into pieces, and preserved in a stoppered bottle. It is much employed, from its great affinity for water, to dry gases and absorb moisture. Chloride of calcium always acquires by fusion a slight but sensibly alkaline reaction from partial decomposition; on which account Liebig prefers the salt strongly dried, but not fused, as the hygrometric agent in organic analysis. Ignited with the sulphates of baryta and strontia, chloride of calcium gives rise to sulphate of lime and the chlorides of barium and strontium. Ten parts of anhydrous alcohol dissolve 7 parts of chloride of calcium, at the boiling-point, and the solution, in cold weather, affords crystals in rectangular scales, which are an alcoholate, containing 2 eq. of alcohol, instead of water of crystallization; $CaCl+2C_4H_6O_2$. Anhydrous chloride of calcium likewise absorbs 4 equivalents of ammoniacal gas, and forms a bulky white powder, $CaCl+4NH_3$, from which the ammonia may be easily expelled again by heat.

A solution of chloride of calcium, when boiled with hydrate of lime, dissolves that substance, and the solution filtered hot, deposits an *oxichloride of calcium*, $3CaO.CaCl+15HO$, in long flat and thin crystals. The salt is decomposed by water and alcohol.

A compound of chloride of calcium with *oxalate of lime* containing water of crystallization, is obtained in good crystals, which are persistent in air, by dissolving oxalate of lime to saturation in hot hydrochloric acid, and allowing the solution to cool. It consists of 1 eq. of each salt, with 7 eq. of water. Oxalate of lime is known to combine with 2 eq. of water, of which 1 eq. appears to remain in this double salt, while the other is replaced by chloride of calcium carrying its 6 eq. of water of crystallization along with it; $CaO.C_2O_3+(HO.CaCl)+6HO$. A similar replacement is observed in the formation of quadroxalate of potassa (p. 164). This salt becomes anhydrous without decomposition at 266° (130° C.) It is decomposed by pure water.

Fluoride of calcium, Fluor-spar; CaF; 38.70 *or* 483.80.—This salt is peculiarly a constituent of mineral veins, and occurs massive, or in transparent crystals which are cubes or octohedrons, and is often of beautiful colours, generally green or purple. It is cut into ornamental forms, and is believed to be the substance of which the *vasa murrina* of the Romans were composed. In minute quantity fluoride of calcium is very generally diffused, being found in the earthy deposit from sea-water when boiled (G. Wilson). It forms a few thousandths of the earth of bones, and a somewhat larger proportion of the enamel of the teeth: in fossil bones the proportion of fluoride of calcium is considerably greater (J. Middleton, Mem. Chem. Soc. ii. 134). It is dissolved to a small extent by water containing carbonic acid, like the other insoluble salts of lime; its density varies from 3.14 to 3.17. When heated gently, on a plate of metal, it becomes luminous in the dark for a short time; the phosphorescent property may be restored by passing electric sparks through the crystal (Griffiths). Fluoride of calcium is obtained in a granular condition, when hydrofluoric acid is neutralized by freshly precipitated carbonate of lime. But when a neutral salt of lime is mixed with a soluble fluoride, the fluoride of calcium appears as a translucent gelatinous mass. This fluoride, whether artificial or natural, is not decomposed by sulphuric acid at a low temperature, but imbibes that acid, and forms a thick ropy liquid. At 104° (40° C.), this mixture begins to decompose, and emits hydrofluoric acid. Fluoride of calcium resists the action of a solution of hydrate of potassa, but is easily decomposed in the dry way by fusion with carbonate of potassa, and fluoride of potassium is formed.

SALTS OF LIME.

Carbonate of lime; $CaO.CO_2$; 50, *or* 625.—This is one of the most abundantly diffused salts in nature, forming the basis of limestones, marbles, marls, coral-reefs, shells, &c. It is anhydrous, and occurs in two incompatible crystalline forms, the rhomboidal crystal of Iceland spar and calc-spar, which, with its numerous modifications, is much the most abundant, and the six-sided prism of arragonite, isomorphous with carbonate of strontia, which last may be readily recognized by falling to powder when heated. The grains of this powder have the form of calc-spar. The density of carbonate of lime in these two forms is sensibly different, that of calc-spar being 2.719, and of arragonite 2.949 (G. Rose). Carbonate of lime consists of 56 lime and 44 carbonic acid in 100 parts.

Carbonate of lime may also be obtained in the state of a hydrate by heating together very slightly 1 part of hydrate of lime, 3 parts of sugar, and 6 parts of water, filtering the solution, and leaving it exposed in a shallow vessel. In twenty-four hours crystals appear upon the surface of the liquid, and in fifteen days the whole lime is generally converted into hydrated carbonate, in the form of sharp transparent rhombs. The carbonic acid is absorbed from the atmosphere. These crystals contain 5 eq. of water; by boiling them in anhydrous alcohol, a second definite hydrate is obtained containing 3 eq. of water, as ascertained by Pelouze. The first of these hydrates has also been found native in a running stream, by Scheerer. The two hydrates of carbonate of lime correspond in composition with two crystalline hydrates of carbonate of magnesia.

Carbonate of lime is considered an insoluble salt, although, according to Fresenius, one part of carbonate of lime dissolves in 8834 parts of boiling water, and in 10601 parts of water at ordinary temperatures: the solution is sensibly alkaline to test-paper. When recently precipitated, carbonate of lime is much more soluble in salts of ammonia: the solution of carbonate of lime in hydrochlorate of ammonia in excess is completely resolved by spontaneous evaporation into chloride of calcium and carbonate of ammonia, which escapes. Sea-water appears to be essentially alkaline from the presence of carbonate of lime, a circumstance calculated, therefore, to prevent the accumulation in the sea of ammonia in the form of fixed salts, and to cause the restoration of that base to the atmosphere. Carbonate of lime is soluble in water containing carbonic acid, and is generally present in the water of wells, and in some mineral waters to a considerable extent. It is deposited from the latter, when exposed to air in a gradual manner and in possession of a crystalline structure, forming stalactites and stalagmites in mountain caverns, and calcareous petrifications, when it flows over wood and other organic and destructible matters, of which it preserves the form. When a current of carbonic-acid gas is passed through lime-water, the greater portion, but not the whole, of the carbonate of lime first precipitated is re-dissolved by the excess of carbonic acid. This solution yields on evaporation the anhydrous carbonate, and no crystalline bicarbonate of lime has been obtained. Carbonate of lime is decomposed with effervescence by acids. At a red heat it parts with carbonic acid, and is converted into quicklime in the manner already described.

A crystalline mineral was discovered by Boussingault at Merida in America, which he ascertained to be a double carbonate of soda and lime, with 5 eq. of water, and named *gaylussite*, in honour of Gay-Lussac. It may be made anhydrous by heat, and its two salts are then separated by water.

The hardness of well and river-water, so far as it is due to carbonate of lime in solution, may be removed by a proper addition of lime-water, the free carbonic acid becoming carbonate of lime, and precipitating together with the portion of carbonate of lime formerly held in solution; colouring and other organic matter is carried down at the same time.[1] This elegant process has been found to act satisfactorily on a large scale. The proportion of carbonate of lime, where it is the only alkaline substance in solution, may be determined with great accuracy by neutralizing 8750 grains of the water (one pint), by means of a normal acid solution containing 0.4562 per cent. of hydrochloric acid (this is 319.37 grs. of HCl in one gallon, or 70000 grs. of water, or as much acid as would neutralize one ounce or 437.5 grs.

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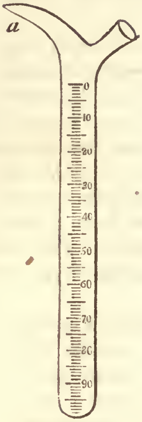
[1] Professor Clark: Repertory of Patent Inventions, October 1841; a pamphlet entitled "A New Process for Purifying Waters supplied to the Metropolis," published by R. and J. E. Taylor; and "On the Examination of Water for its Hardness," Pharmaceutical Journal, vi. 526. The instruments and test-liquids required in the examination of waters by Prof. Clark's method may be obtained at Mr. Griffin's, in Baker street, London.

Fig. 185.



of carbonate of lime). This test-acid is prepared by means of pure carbonate of soda, as in the process of alkalimetry (page 386), or from the analysis of the dilute acid by nitrate of silver. The measured quantity of water is placed in an evaporating basin, and being found alkaline by delicate red litmus-paper, the normal acid is added from the small burette (fig. 185) graduated into ten-grain measures, each of which is subdivided into five, till the point of neutralization is reached, the liquid being heated towards the end of the operation. A small portion of 30 or 40 grains of the water is transferred to a small conical wine-glass, and the test-paper left in it for several minutes, to obtain the indication of alkalinity. To save time, a series of six of these wine-glasses is conveniently employed, each containing a sample of the water after successive additions of the test-acid. Each ten-grain measure of the acid required indicates 1 grain of carbonate of lime in 1 gallon of the water, or 0.000014286 per cent. of carbonate of lime. By such means a minutely accurate determination of alkalinity may be obtained; one-hundredth of a grain of carbonate of lime in a pint of water is thus observed. (Prof. Clark).

Sulphate of lime, Gypsum; $CaO.SO_3 + 2HO$; 68 + 18 *or* 850 + 225. — This salt precipitates as a bulky and gritty powder, when sulphuric acid is added to a soluble salt of lime. Sulphate of lime appears to have nearly the same degree of solubility at all temperatures, and requires 460 parts of water for solution, according to Bucholz, or 380 parts of cold, and 388 parts of boiling water, according to Geise. It occurs in nature in well-formed crystals, and also in large crystalline masses, forming beds of gypsum; a mineral which contains 2 eq. of water, and of which the density is 2.322 (Royer and Dumas). Prof. Johnston likewise obtained small prismatic crystals of sulphate of lime, deposited in a steam-boiler, which contain only half an equivalent of water $2(CaO.SO_3) + HO$. Sulphate of lime occurs in a crystalline form, without water, forming the mineral *anhydrite,* of which the density is about 2.96. Sulphate of lime fuses at a strong red heat, without decomposition, and on cooling assumes the crystalline form of the last mineral. To form plaster of Paris, gypsum, in pieces about the size of a pigeon's egg, is heated in an oven till it is nearly anhydrous, and then reduced to a powder. When this is made into a paste with a little water, it forms a hard coherent mass, or sets, in a minute or two, with a slight evolution of heat. This artificial hydrate, or *stucco,* has the same composition as native gypsum. If sulphate of lime has been heated above 300°, in drying, it refuses to set afterwards when mixed with water.

The powder of hydrated gypsum solidifies also when mixed with a solution of potassa, or various salts of potassa, such as the carbonate, bicarbonate (in this case with violent effervescence), sulphate, and silicate, but not with the chlorate or nitrate of potassa, nor with any salt of soda. Double salts are probably formed, as it is the alkaline salts only which are capable of forming double salts, and are considered bibasic by M. Herhardt, that possess the remarkable property in question (Emmet, Am. Journ. of Scien., xxiii. 209). [*See Supplement,* p. 816.]

Hyposulphite of lime is formed by transmitting sulphurous acid through sulphide of calcium, suspended in water, till the solution is neutral and colourless. The solution is decomposed when heated above 140° (60° C.) into sulphur and sulphite of lime. If evaporated below that temperature, it yields large hexagonal prisms of hyposulphite of lime, on cooling, which are colourless. They contain 5 eq. of water, and are persistent in air. The same salt may be obtained very economically by exposing to air the waste-lime of the dry-lime gas purifiers.

Nitrate of lime is a highly deliquescent salt, which crystallizes with 6 eq. of water, like the nitrates of the magnesian class. It is soluble in alcohol.

Phosphates of lime.—On adding chloride of calcium to the tribasic subphosphate of soda, a corresponding phosphate of lime precipitates in bulky gelatinous flakes, of which the formula is $3CaO.PO_5$. This phosphate occurs in nature in combination with fluoride of calcium in the form of hexagonal prisms, in the minerals *apatite* and *moroxite*. The formula of apatite is $CaF + 3(3CaO.PO_5)$. The native phosphates of lead occur in the same form, with chloride of lead in the place of fluoride of calcium. *Hedyphan* is the same mineral, in which a portion of phosphoric acid is replaced by arsenic acid. [*See Supplement*, p. 816.]

Another tribasic phosphate of lime is obtained on adding the solution of common phosphate of soda, drop by drop, to chloride of calcium. This precipitate is slightly crystalline. Its formula, exclusive of its water of crystallization, is $HO.2CaO.PO_5$. Again, when a solution of phosphate of ammonia, supersaturated with ammonia, is treated with a solution of chloride of calcium, till about one-half of the phosphoric acid is precipitated, the precipitate contains 51.263 per cent of lime, and corresponds to the formula $8CaO.3PO_5$ (Berzelius). A biphosphate of lime is also described by Berzelius, obtained on evaporating a solution of any of the preceding salts in nitric acid to the point of crystallization, of which the probable formula is $2HO.CaO.PO_5$. There also exist a pyrophosphate and metaphosphate of lime. The insoluble phosphates of lime are soluble in water containing carbonic acid. It is possibly in this manner that phosphate of lime is dissolved by the alkaline animal fluids.

Hypochlorite of lime; Chloride of lime; Bleaching powder.—This compound, remarkable for its valuable applications in the arts, is generally prepared by exposing hydrate of lime, from the purest lime, to chlorine-gas, the latter being supplied so gradually as to prevent the heat, occasioned by the combination, from rising above 62°. Chlorine is not absorbed by quicklime, nor by the carbonate of lime. When dried at 212°, hydrate of lime, I find, absorbs afterwards little or no chlorine; but dried over sulphuric acid, without heat, it is, on the contrary, in the most favourable condition for becoming chloride of lime. A dry, white, pulverulent compound is obtained by exposing the last hydrate to chlorine, which contains 41.2 to 41.4 chlorine in 100 parts; but of this chlorine about 39 parts only are available for bleaching, owing to 2 parts of that element going to the formation of chloride of calcium and chlorate of lime. A slight addition of moisture to hydrate of lime does not increase the proportion of chlorine absorbed, and renders the compound less stable. The above appears to be the maximum absorption of chlorine by dry hydrate of lime, and is greater than it would be advisable to attempt in the manufacture of bleaching powder, owing to the occurrence of the partial decomposition adverted to. Yet this proportion is considerably short of 1 eq. of chlorine to 1 of hydrate of lime, which are 48.57 chlorine and 51.43 hydrate of lime, in 100 parts. The excess of lime appears to be useful in adding to the stability of the compound. Labarraque mixes the hydrate of lime with $\frac{1}{20}$th of its weight of chloride of sodium, by which means the absorption of chlorine is greatly promoted. The bleaching powder of commerce may contain, when newly prepared, about 30 per cent. of chlorine; but after being kept for several months, the proportion of available chlorine is found more frequently below than above 10 per cent., so much does it deteriorate by keeping.

The reaction which occurs in the formation of hypochlorite of lime is represented as follows:—

$$2CaO \text{ and } 2Cl = Ca.Cl \text{ and } CaO.ClO.$$

Or the product is a mixture of chloride of calcium and hyperchlorite of lime.

The same compound is obtained in solution by transmitting a stream of chlorine-gas through hydrate of lime suspended in water. The lime then absorbs a full equivalent of chlorine, and dissolves entirely.

Ten parts of water take up the bleaching combination from one part of dry chloride of lime, leaving undissolved the hydrate of lime contained in excess. The solution has a slight odour of hypochlorous acid, a rough astringent taste, and alkaline reaction. It destroys most organic matters containing hydrogen, including colouring matters. But its bleaching action is not instantaneous, unless an acid be added to it, which liberates the chlorine. Hence, when Turkey-red cloth, having a pattern printed upon it with tartaric acid thickened by gum, is immersed for about one minute in this solution, it comes out with the colour discharged where the acid was present, but elsewhere uninjured. In this manner white figures are produced upon a coloured ground. The solution of chloride of lime also absorbs and destroys contagious matters in the atmosphere, and is slowly decomposed by carbonic acid, with escape of chlorine. The powder or its solution, when heated, or when kept for a considerable time, undergoes decomposition; 18 eq. of chlorine then leaving 17 eq. of chloride of calcium, and 1 eq. of chlorate of lime, and disengaging 12 eq. of oxygen-gas, according to the observations of M. Morin.

CHLORIMETRY.

The bleaching power of hypochlorite of lime is often estimated by the quantity of a solution of sulphate of indigo, which a constant weight of the substance can deprive of its blue colour, or render yellow. But as the indigo-solution alters by keeping, this method is not unobjectionable. A more exact method is that in which sulphate of iron is used. This method reposes upon the circumstance that the chlorine of hypochlorite of lime converts a salt of the protoxide into a salt or the sesquioxide of iron; half an equivalent, or 222 parts of chlorine, effecting that change upon a whole equivalent, or 1728 parts of cr. protosulphate of iron. Protoxide of iron is convertible into sesquioxide by half an equivalent of oxygen, which the half equivalent of chlorine may be supposed to supply, by decomposing water, in becoming hydrochloric acid. It follows, by proportion, that 10 grains of chlorine are capable of peroxidizing 77.9 grains of cr. protosulphate of iron.

A few ounces of good crystals of protosulphate of iron are reduced to powder, and dried by strong pressure between folds of cloth; the salt may afterwards be preserved in a bottle without change. In a chlorimetric experiment, 78 grains (equivalent to 10 grains of chlorine) of this salt are dissolved in about two ounces of water, which may be acidulated by a few drops of sulphuric or hydrochloric acid. Fifty grains of the chloride of lime to be examined are dissolved in about two ounces of tepid water, by rubbing them together in a mortar, and the whole poured into the alkalimeter (page 386), which is afterwards filled up to 0 on the scale, by the addition of water, and the whole mixed by inverting the alkalimeter upon the palm of the hand. The solution of chloride of lime, being thus made up to 100 measures, is poured gradually into the sulphate of iron, till the latter is completely peroxidized, and the number of measures of chloride required to produce that effect observed. The change in the degree of oxidation of the iron-solution is discovered by means of red prussiate of potassa, which gives a precipitate of Prussian blue with a salt of the protoxide of iron only, and not with a salt of the sesquioxide. By means of a glass-stirrer, a white stoneware plate is spotted over with small drops of the prussiate. A drop of the iron-solution is mixed with one of these, after every addition of chloride of lime, and the additions continued, so long as a deep blue precipitate is produced. The liquid may continue to be coloured green by the iron-salt, but that is of no moment. The richer the specimen of chloride of lime is in chlorine, the fewer measures of its solution are required to peroxidize the iron, the number of measures containing 10 grains of chlorine always producing that effect. The quantity of chlorine in the fifty grains of bleaching powder is now known, being ascertained by the proportion, as *m* measures (the number poured out by the alkalimeter) is to 10 grains of chlorine, so 100 is to the total grains of chlorine. In a particular experiment the 78 grains of sulphate of iron required 72 measures of the bleaching solution. Hence, as 72 is to 10, so 100 is to 13.89 chlorine in 50 grains of the chloride of lime. The quantity of chlorine in 100 grains of the chloride, or the percentage of chlorine, is obtained by doubling that number; and was therefore, in this instance, 27.78 per cent., or 28 per cent. The arithmetical process may always be reduced to that of dividing 2000 by the number of measures poured from the alkalimeter: thus in the last example —

$$\frac{2000}{72}=27.78.$$

SECTION IV.

MAGNESIUM.

Eq. 12.2, *or* 152.5; Mg.

To obtain magnesium, sodium in a test-tube of hard glass is covered by fragments of anhydrous chloride of magnesium, and heated to redness by a lamp. The alkaline metal unites with chlorine, with strong ignition. After extracting the chloride of sodium by means of water, the magnesium remains in little globules, which may be reunited by fusing them under a stratum of chloride of potassium at a moderate red-heat. [*See Supplement*, p. 817.]

Magnesium has the colour and lustre of silver; it is very ductile, and capable of being beaten into thin leaves, fuses at a gentle heat, and crystallizes in octohedrons. Magnesium is oxidized superficially by moist air, but undergoes no change in dry air or oxygen. Heated to redness, it burns with great brilliancy, forming magnesia. It is evidently more analogous to zinc than to the preceding metals.

Magnesia; MgO; 20.2, *or* 252.5. — This is the only known oxide of magnesium. As usually prepared, by a gentle but long calcination of the artificial carbonate of magnesia, it forms a white soft powder, the *magnesia usta* of pharmacy. Magnesia is of density 3.61 after ignition in a porcelain-furnace (H. Rose), and highly infnsible. It combines with water, but with much less avidity than lime does, forming a protohydrate. The native hydrate of magnesia has the same composition, and so has the compound obtained by precipitating magnesia from its soluble salts (by means of hydrate of potassa) and washing well, when dried either without heat or at 212°. These preparations have a silky lustre and a softness to the touch, characteristic of magnesian minerals, such as is observed in asbestos and soapstone.

According to M. Fresenius, magnesia requires for solution 55368 parts of water, either boiling or at ordinary temperatures; the solution is feebly alkaline, and gives a sensible precipitate on the addition of phosphate of soda, followed by ammonia. When this earth and its salts are moistened with nitrate of cobalt, and strongly ignited before the blow-pipe, they assume a fine rose-colour: phosphate of magnesia takes more of a violet tint. Magnesia is precipitated from its soluble salts by lime-water, but is still a strong base capable of neutralizing acids perfectly. Ammonia never throws down more than half of the magnesia from the solution of a salt of magnesia, owing to the formation of a soluble double salt of magnesia and ammonia; and the flaky precipitate produced by ammonia in the solution of a salt of magnesia disappears again completely on the addition of hydrochlorate of ammonia. Magnesia is precipitated from its salts by the carbonates, but not by the bicarbonates, of potassa and soda. It is most correctly estimated by precipitation by the phosphate of soda with caustic ammonia, washing with water containing hydrochlorate of ammonia, and igniting the precipitated phosphate of magnesia and ammonia; the whole magnesia being ultimately obtained in the form of bibasic phosphate of magnesia, $2MgO.PO_5$.

Chloride of magnesium, made by neutralizing carbonate of magnesia with hydrochloric acid, crystallizes in thin needles, which contain 6 eq. of water, and are highly deliquescent. When we attempt to make this salt anhydrous by heat, hydrochloric acid escapes, and magnesia remains. But the pure chloride of magnesium, which is employed in preparing the metal, may be obtained by dividing a quantity of hydrochloric acid into two equal portions, neutralizing one with magnesia and the other with ammonia, mixing and evaporating these two solutions to dryness, when an anhydrous double chloride of magnesium and ammonia is formed. On heating this salt to redness in a covered porcelain-crucible, sal-ammoniac sublimes, and chloride of magnesium remains in a state of fusion, which becomes a translucent, crystalline mass on cooling. This chloride is decomposed by oxygen, which, at a high temperature, displaces its chlorine, and magnesia is formed. According to M. Poggiale, the chloride of magnesium forms with chloride of sodium a double salt, which has the formula $2MgCl.NaCl+2HO$.

Carbonate of magnesia.—This salt occurs native, and then always in the anhydrous condition, as a white, hard, compact mineral of an earthy fracture, which is known as *magnesite*, and sometimes in rhombohedral crystals, similar to those of carbonate of lime. It is prepared artificially by precipitating a soluble salt of magnesia, by means of carbonate of potassa at the boiling-point. The precipitate is diffused in pure water, and a stream of carbonic acid sent through it, by which the carbonate of magnesia is dissolved. On allowing this solution to evaporate spontaneously, the excess of carbonic acid escapes, and carbonate of magnesia is deposited in small hexagonal prisms with right summits. These crystals contain 3 eq. of water. They effloresce in dry air, and then lose 2 eq. of water, according to my own observations. Carbonate of magnesia has also been obtained in crystals, with 5 eq. of water, from the solution in carbonic acid, at a low temperature. There are, consequently, three hydrates of this salt, of which the formulæ are—

$$MgO.CO_2.HO;$$
$$MgO.CO_2.HO+2HO;$$
$$MgO.CO_2.HO+4HO.$$

The fact that the carbonate of magnesia dissolves in carbonic acid-water is not to be held as a proof of the existence of a bicarbonate of magnesia. Various insoluble salts, such as phosphate of lime and fluoride of calcium, dissolve in the same liquid, which appears to possess a specific solvent power. In the analogous solution of carbonate of lime in carbonic acid-water, the proportion of the carbonate was found by Berthollet to have a variable and indefinite relation to the acid. On theoretical grounds, supersalts, of the ordinary constitution, of magnesia, and the magnesian family of oxides, are not to be expected, as they would be double salts of water and another magnesian oxide.

Magnesia alba, or the subcarbonate of magnesia of pharmacy, is prepared by precipitating a boiling solution of sulphate of magnesia or chloride of magnesium, by means of carbonate of potassa. Carbonate of soda is not so suitable as a precipitant of magnesia, as a portion of it is apt to go down in combination with the magnesian carbonate, but it may be used provided the quantity applied be less than is required to decompose the whole magnesian salt in solution. Magnesia alba, when washed with hot water, is very white, light, and bulky. A portion of carbonic acid is lost, the magnesia not being in combination with a full equivalent of that acid. Berzelius found magnesia alba to contain, in 100 parts, 35.77 carbonic acid, 44.75 magnesia, and 19.48 water; or to consist of 3 eq. of carbonic acid, 4 eq. of magnesia, and 4 eq. of water. It is viewed as a combination of 3 eq. of protohydrated carbonate of magnesia with 1 eq. of protohydrate of magnesia; of which the formula is $3(MgO.CO_2.HO)+MgO.HO$. This compound requires 2500 parts of cold, and 9000 of hot water for solution (Dr. Fyfe).

Bicarbonate of potassa and magnesia.—This salt was formed by Berzelius by mixing a solution of nitrate of magnesia or chloride of magnesium (not the sulphate of magnesia) with a saturated solution of bicarbonate of potassa in excess, and allowing the liquor to rest. In the course of a few days, the double salt is deposited in large regular crystals. These crystals are insipid; insoluble in pure water, but slowly decomposed by it. The composition of this salt corresponds with 1 eq. of potassa, 2 of magnesia, 4 of carbonic acid, and 9 of water. It contains the elements of 1 eq. of a hydrated bicarbonate of potassa, and of 2 eq. of hydrated carbonate of magnesia.

$$\left\{\begin{array}{l} MgO.CO_2.HO+2HO \\ HO.CO_2.(KO.CO_2)+2HO \\ MgO.CO_2.HO+2HO. \end{array}\right.$$

It appears an association, or compound, of three salts of similar constitution. This salt, I find, loses 8HO at 212°, or all its combined water, except the single basic equivalent of the bicarbonate of potassa. A corresponding bicarbonate of soda and magnesia also exists.

Dolomite, a magnesian limestone, very extensively diffused in nature, is a mixture or combination of the carbonates of lime and magnesia, having the crystalline form of calc-spar. The two salts unite in all proportions, but are most frequently found in the proportion of single equivalents. It is remarkable that when this rock is exposed to the solvent action of water containing carbonic acid, the carbonate of lime is dissolved exclusively, and a magnesian limestone remains in the form of a porous and crystalline mass. It is not unusual to find whole mountains of magnesian limestone thus altered.

Sulphate of magnesia; $MgO.SO_3.HO+6HO$; $60.2+63$, *or* $752.5+787.5$.—This salt exists in many mineral springs, in the waters of Epsom, of Seidlitz in Bohemia, &c., from which it was first procured by evaporation. It is now obtained from the bittern of sea-water, which consists principally of chloride of magnesium and sulphate of magnesia, and is converted wholly into sulphate by the addition of sulphuric acid. Or magnesia is precipitated from sea-water confined in a tank, by means of hydrate of lime, and the earth thus obtained afterwards neutralized by sulphuric acid. Magnesian limestone is also had recourse to for magnesia. It is burned and slaked with water, to obtain it in a divided state, and then neutralized by sulphuric acid. The mixed sulphates are easily separated, that of lime being soluble to a minute extent only, while that of magnesia is highly soluble in water. A solution of sulphate of lime is also decomposed by carbonate of magnesia, with the formation of sulphate of magnesia; and this reaction is often witnessed in beds of magnesian limestone, when water containing sulphate of lime percolates through them.

The crystals of sulphate of magnesia are four-sided rectangular prisms, which, when pure, have a slight disposition to effloresce in dry air. One hundred parts of water at 32° dissolve 25.76 parts of the anhydrous salt, and for every degree above that temperature they take up 0.26564 part additional (see Gay-Lussac's table of the solubility of salts, at page 178). The solution has a bitter disagreeable taste, which is characteristic of all the soluble salts of magnesia. It is not precipitated in the cold by the alkaline bicarbonates, by common carbonate of ammonia, nor by oxalate of ammonia if the solution of sulphate of magnesia be dilute. This salt crystallizes at 32° with 12HO (Fritzsche); it is also generally stated to crystallize about 70°, with 6HO.

Sulphate of magnesia loses 6HO considerably under 300°, but retains 1 eq. of water even at 400.° The last equivalent is replaced by sulphate of potassa, forming the double sulphate of magnesia and potassa, which is considerably less soluble than the sulphate of magnesia, and crystallizes with 6HO. Sulphate of magnesia unites directly with sulphate of ammonia also, at the ordinary temperature, and with sulphate of soda above 100° (Mr. Arrott).

Sulphate of magnesia, when ignited in contact with charcoal, leaves magnesia with very little sulphide of the metal; it is the last of the earths which exhibits any analogy of this kind to the alkalies. The hydrosulphate of sulphide of magnesium is soluble in water, and appears to be formed when sulphate of magnesia is precipitated by sulphide of barium.

Hyposulphate of magnesia forms crystals, which are persistent in air, very soluble, and contain 36.77 per cent. or 6 eq. of water, like the following salt.

Nitrate of magnesia is a very soluble and highly deliquescent salt. It crystallizes with $6HO$.

Phosphate of magnesia is formed on mixing cold solutions of common phosphate of soda and sulphate of magnesia, and allowing to stand for 24 hours. The salt appears in tufts of slender prisms, which effloresce in dry air. They are soluble in about 1000 times their weight of water. The composition of this salt, which I carefully examined, may be expressed by the following formula — $HO.2MgO.PO_5 + 2HO + 12HO$. (Phil. Trans. 1837.)

Phosphate of magnesia and ammonia. — This is the well-known granular precipitate which appears when a tribasic phosphate and a salt of ammonia are dissolved together, and any salt of magnesia is added to the mixture. Its formation is had recourse to as a test of the presence of magnesia. Although insoluble in a liquid containing salts, it is so soluble in pure water that it cannot be washed without sensible loss. It is readily dissolved by acids. The same substance forms the basis of the variety of urinary calculus known as the ammoniaco-magnesian phosphate. It is a tribasic phosphate, of which the 3 eq. of base are 1 eq. of oxide of ammonium and 2 eq. of magnesia, with 12 eq. of water of crystallization: ten of the latter may be expelled without any loss of ammonia. The formula of this salt is therefore $NH_4O.2MgO.PO_5 + 2HO + 10HO$. The same salt was found in crystals of considerable magnitude, by Dr. Ulex, in the old soil of the city of Hamburgh, and named *struvite*, as a new mineral species. It has also been found in guano, and hence named *guanite* by Mr. Teschemacher. Dr. Otto has observed a corresponding tribasic phosphate of protoxide of iron and ammonia, which contains only 2 eq. of water; and also an arseniate of manganese and ammonia, of which the water of crystallization appears to be the same as that of the phosphate of magnesia and ammonia. By igniting, without fusing, phosphate of magnesia with a small quantity of carbonate of potassa, an insoluble double salt of similar constitution, $2MgO.KO.PO_5$, was obtained by H. Rose. Corresponding double phosphates, containing 2 eq. of lime, baryta, and strontia, in the place of the 2 eq. of magnesia, were prepared in a similar manner.

Borate of magnesia. — The neutral salt was obtained by M. Wöhler, in the form of crystals, by heating a mixture of the solutions of sulphate of magnesia and borax to the boiling point, so as to form a precipitate, which is re-dissolved on cooling, and leaving the liquid at a temperature only a few degrees above 32° for some months. There were formed on the sides of the vessel thin crystalline needles, transparent, brilliant, hard, and having much of a mineral character, insoluble in hot or cold water, and having the composition $MgO.BO_3 + 8HO$. Boracic acid forms also an insoluble triborate of magnesia, $3MgO.BO_3 + 9HO$; a soluble terborate, $MgO.3BO_3 + 8HO$; and a soluble sexborate, $MgO.6BO_3 + 18HO$.

The mineral *boracite*, which occurs in the cube and its allied forms, is an anhydrous compound of magnesia and boracic acid, in the ratio of 3 eq. of magnesia to 4 eq. of boracic acid, which is represented by $MgO.2BO_3 + 2(MgO.BO_3)$. This mineral becomes electrical by heat. The rare mineral, *hydroboracite*, is, according to Hess, a compound of a borate of lime and borate of magnesia, in both of which the acid and base are in the same ratio as in boracite, with 18 eq. of water.

Silicates of magnesia. — Magnesia is found combined with silicic acid in various proportions, forming several mineral species, of which the formulæ are as follows:—

Steatite..................................	$5(MgO.SiO_3) + 2HO$.
Meerschaum	$MgO.SiO_3 + 2HO$.
Picrosmine and pyrallolite...........	$6MgO.4SiO_3 + 3HO$.
Peridote (olivine, or chrysolyte)....	$3MgO.SiO_3$.
Serpentine (hydrate of magnesia with subsilicate of magnesia......	$2(3MgO + 2SiO_3) + 3(MgO.2HO)$.
Pyroxene or augite (silicate of lime and magnesia)	$3CaO.2SiO_3 + 3MgO.2SiO_3$.
Amphibole, or hornblende (silicate of lime and magnesia)............	$CaO.SiO_3 + 3MgO.2SiO_3$.

In these minerals, particularly the two last, the magnesia is often replaced, in whole or in part, by protoxide of iron, which gives them a green, and sometimes black colour. Fine crystals of pyroxene are often found among the scoriæ of blast-furnaces. Serpentine is easily decomposed by acids, and may be employed in the preparation of sulphate of magnesia. A variety of other minerals are formed of silicic acid and magnesia, anhydrous or hydrated; such as talc, metaxite, &c.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION I.

ALUMINUM.

Eq. 13.7 *or* 171.2; Al.

This element is named from *alumen*, the Latin term for alum, which is a double salt, consisting of sulphate of alumina and sulphate of potassa.

Like the preceding metal, aluminum is obtained from its chloride by the action of potassium. In order to diminish the violence of the reaction, M. Wöhler recommends that about 20 grains of perfectly dry potassium be introduced into a small platinum-crucible, which is placed within another larger crucible, also of platinum, containing the anhydrous chloride of aluminum. The cover of the larger crucible is then fastened down by an iron-wire, and heat applied with caution. The aluminum is afterwards separated from the chloride of potassium, with which it is mixed, by digesting the crucible and its contents in a considerable quantity of cold water. The metal appears as a grey powder, resembling spongy platinum, but is seen in a strong light, while suspended in water, to consist of small scales or spangles having the metallic lustre. It is not a conductor of electricity when in this divided state, but becomes one when its particles are approximated by fusion. Wöhler finds that iron resembles aluminum in that respect. [*See Supplement*, p. 818.]

Aluminum has no action upon water at the usual temperature, but decomposes it to a small extent at the boiling temperature, with the evolution of hydrogen. It undergoes oxidation more rapidly in solutions of potassa, soda, and ammonia, and the resulting alumina is dissolved by these alkalies. Aluminum requires for fusion a temperature higher than that at which cast-iron melts. Heated in open air, it takes fire and burns with a vivid light, and in oxygen-gas with the production of so much heat as to fuse the alumina, which then has a yellowish colour, and is equal in hardness to the native crystallized aluminous earth, corundum.

Alumina; Al_2O_3: 51.4 *or* 642.5.—This earth is the only degree of oxidation of which aluminum is susceptible, so far as is known at present. In its constitution, alumina is presumed to resemble sesquioxide of iron, because it occurs crystallized in the same form as the native sesquioxide of iron, and the salts into which it enters are strictly isomorphous with the corresponding salts of that oxide. To 3 eq. of oxygen it must, therefore, contain 2 eq. of metal, such being the composition of sesquioxide of iron. Aluminum is not known to enter into combination in any other proportion than that of two equivalents of the metal to three of the halogenous constituent. [*See Supplement*, p. 819.]

Alumina occurs in a state of purity, with the exception of a trace of colouring matter, in two precious stones, the *sapphire* and *ruby*; the first of which is blue, and the other red. They are not inferior in hardness to the diamond. Their density is from 3.9 to 3.97. Alumina may be obtained by calcining the sulphate of alumina and ammonia, or ammoniacal alum, very strongly. But alumina so prepared is insoluble in acids. It is obtained in the state of a hydrate from common alum by dissolving the latter in boiling water, and adding a solution of ammonia (or better, of the carbonate of ammonia), and boiling. This earth is still more perfectly precipitated by the hydrosulphate of ammonia, according to MM. Malaguti and Durocher. The precipitate, which is white, gelatinous, and very bulky, must be carefully washed, by mixing it several times with a large quantity of distilled water, allowing it to settle, and pouring off the clear liquid. By drying in air, alumina is reduced to a few hundredths of the bulk of the humid mass. It is still a hydrate, but, when ignited at a high temperature, it gives anhydrous alumina. One hundred parts of alum furnish 10.3 parts of alumina.

Alumina is white and friable. It has no taste, but adheres to the tongue. Before the oxihydrogen-blow-pipe it melts into a colourless glass. After being ignited, it is dissolved by acids with great difficulty. It is highly hygrometric, condensing about 15 per cent. of moisture from the atmosphere in damp weather. If ignited alumina contains a small portion of magnesia, it becomes warm when moistened with water: this property is very sensible, even when the proportion of magnesia does not exceed half a per cent. It appears to be due, not to chemical combination, but to heat disengaged by humectation,—a phenomenon first observed by Pouillet.

The hydrate of alumina, when moist, is gelatinous and semi-transparent, like starch, but dries up into gummy masses. It is completely insoluble in water, but is readily dissolved by acids, and also by the fixed alkalies; this earth standing in the relation of an acid to the stronger bases. Caustic ammonia dissolves it only in small quantity. The hydrate of alumina is deposited in crystals when the solution of this earth in potassa is allowed to absorb carbonic acid slowly from the air. The crystals are white and transparent at the edges, and contain 3 eq. of water, which they do not lose at 212°. The mineral *gibsite* is a native hydrate of alumina of the same composition, $Al_2O_3 + 3HO$. Another native hydrate exists, containing less water, $Al_2O_3 + 2HO$. It is called *diaspore* by mineralogists, from decrepitating and falling to powder when heated,—a property which the artificial hydrate in gummy masses likewise exhibits.

Hydrated alumina has a peculiar attraction for organic matter, which it withdraws from solution; and hence this earth is apt to be coloured when washed with water not absolutely pure. This affinity is so strong, that, when digested in solutions of vegetable colouring matters, alumina combines with and carries down the colouring matter, which is removed entirely from the liquid, if the alumina is in sufficient quantity. The pigments called *lakes* are such aluminous compounds. The fibre of cotton, when charged with this earth, attracts and retains with force the same colouring matters. Hence the great application of aluminous salts in dyeing, to impregnate cloth or yarn with alumina, and thus enable it to fix the colouring matter, and produce a fast colour. Alumina is then said to be a mordant: binoxide of tin and sesquioxide of iron have an equal attraction for organic colouring matters.

Alumina, it will be observed, is not a protoxide, and is greatly inferior to the preceding earths in basic power. It is dissolved by acids, but never neutralizes them completely. Hence, alum and all the salts of alumina have an acid reaction. Their solutions have an astringent and sweetish taste, which is peculiar to them. Alumina dissolves, to the extent of several equivalents, in some acids, particularly hydrochloric acid, forming feeble compounds, which are even deprived of a portion of their alumina by filtering them through paper. It is usually supposed that alumina does not combine with some of the weaker acids, such as carbonic acid; and that an alkaline carbonate throws down alumina from alum, and not a carbonate of that earth. The carbonate of ammonia, however, according to Mr. Danson, gives a subcarbonate of alumina, which, dried in vacuo at a low temperature, formed a light bulky powder, having the composition $3Al_2O_3.2CO_2 + 16HO$. Alumina dissolves readily in solution of potassa or soda, forming compounds in which it must play the part of an acid. The aluminate of potassa is deposited, on evaporating a solution of alumina in potassa, in white granular crystals, sweet to the taste, and having a strongly alkaline reaction: its formula is $KO.Al_2O_3$, according to M. Fremy. Such combinations occur in nature: *spinell*, a very hard mineral crystallizing in octohedrons, being an aluminate of magnesia, $MgO.Al_2O_3$; and *gahnite*, an aluminate of zinc, $ZnO.Al_2O_3$.

Sulphide of aluminum is formed by burning the metal in the vapour of sulphur. It is a black semi-metallic mass, which is rapidly transformed, by contact with water, into alumina and hydrosulphuric acid. Hydrosulphate of ammonia has the same effect upon the solution of a salt of alumina as ammonia has itself, neutralizing the acid of the salt, and throwing down alumina, while hydrosulphuric acid escapes.

Chloride of aluminum; Al_2Cl_3; 133.9 *or* 1673.75.—When alumina is dissolved in hydrochloric acid, it is to be supposed that water and a chloride of the metal are formed; $3HCl$ and $Al_2O_3 = Al_2Cl_3$ and $3HO$. The solution, when concentrated by spontaneous evaporation in a very dry atmosphere, yields crystals, which Bonsdorff found to contain 12 eq. of water. But it generally forms a saline mass, which deliquesces quickly in the air. When it is attempted to make this salt anhydrous by heat, the chlorine goes off in the form of hydrochloric acid, and pure alumina is left.

The anhydrous chloride was discovered by Oersted, who made known a method of preparing it which has since had numerous applications. Pure alumina, free from potassa, is intimately mixed with oil and lamp-black, made up into pellets, and strongly calcined in a crucible. The alumina is thus made anhydrous, without being otherwise altered. It is then introduced into a porcelain-tube, which is placed across a furnace and exposed to a red heat. Chlorine-gas, carefully dried, is conducted over the materials in the tube, when, under the conjoint influence of carbon and chlorine, the alumina is decomposed; its oxygen is carried off by the carbon as carbonic-oxide gas, and chlorine unites with the aluminum itself. The chloride of aluminum, being volatile, sublimes and condenses in the cool part of the porcelain-tube. A glass-tube, a little smaller than the porcelain-tube, should be introduced into this part of the latter, which may afterwards be drawn out, containing the condensed chloride. The salt is partly in the state of long crystalline needles, and partly in the form of a firm and solid mass, which is easily detached from the glass.

Chloride of aluminum is of a pale greenish-yellow colour, and to a certain degree translucent. In air it fumes slightly, diffuses an odour of hydrochloric acid, and runs into a liquid by the absorption of moisture. It is very soluble in water, but cannot again be recovered in the anhydrous condition. It is equally soluble in alcohol. Chloride of aluminum combines with hydrosulphuric acid, phosphuretted hydrogen, and also with ammonia.

The *fluoride of aluminum* can only be obtained by dissolving pure aluminum in hydrofluoric acid: it does not crystallize. This fluoride unites in two proportions with fluoride of potassium, for which it has a strong affinity. Both the compounds are gelatinous precipitates, which become white and pulverulent after being washed and dried. Berzelius assigned to them the formulæ, $3KF + Al_2F_3$ and $2KF + Al_2F_3$. Fluoride of aluminum exists in two crystalline minerals, one of which, on account of its transparency, hardness, and brilliancy, is reckoned among the precious stones:—

Topaz	$3(Al_2O_3.SiO_3) + (Al_2O_3 + Al_2F_3)$
Pyknite	$3(Al_2O_3.SiO_3) + Al_2F_3$.

The *sulphocyanide of aluminum* crystallizes in octohedrons, which are persistent in air.

SALTS OF ALUMINA.

Sulphate of alumina; $Al_2O_3.3SO_3 + 18HO$; 171.4 + 162 *or* 2142.5 + 2025.—Obtained by dissolving alumina in sulphuric acid. It crystallizes in thin flexible plates of a pearly lustre, has a sweet and astringent taste, and is soluble in twice its weight of cold water, but does not dissolve in alcohol. When heated, it fuses in its water of crystallization, swells up, and forms a light porous mass, which appears at first to be insoluble in water, but dissolves completely after a time. Heated to redness, it is entirely decomposed; the residue is pure alumina. This salt has been found, in the crystalline form, in the volcanic Island of Milo in the Archipelago. Sulphuric acid and alumina combine in several proportions, but this is considered the neutral sulphate, as it possesses the same number of equivalents of acid as it contains equivalents of oxygen in the base.

Another sulphate of alumina ($Al_2O_3.3SO_3+Al_2O_3$) was obtained by Maus by saturating sulphuric acid with alumina, which contains twice as much alumina as the neutral sulphate. After evaporation, this subsalt presents itself in a gummy mass, which dissolves in a small quantity of water, but is decomposed when the solution is diluted with a large quantity of water, or boiled; in that case the neutral salt remains in solution, and the following salt precipitates. Subtrisulphate of alumina, $Al_2O_3.3SO_3+2Al_2O_3+9HO$, precipitates, on adding ammonia to the sulphate of alumina, as a white insoluble powder. This subsalt forms the mineral *aluminite,* which is found near Newhaven in England, and at Halle in Germany.

Alum; sulphate of alumina and potassa; $KO.SO_3 + Al_2O_3.3SO_3 + 24HO$; 258.4+216, *or* 3230+2700.— Sulphate of alumina has a strong affinity for sulphate of potassa, in consequence of which octohedral crystals of this double salt precipitate when a salt of potassa is added to a strong solution of sulphate of alumina. Alum is a salt of which large quantities are consumed in dyeing. It is prepared by several processes, or derived from different sources. It may be prepared by decomposing clay with sulphuric acid; the decomposition is sometimes effected by igniting pure clay, grinding it afterwards to powder, and mixing it with 0.45 of sulphuric acid, of 1.45 density. This mixture is heated in a reverberatory furnace till the mass becomes very thick; afterwards left to itself for at least a month, and then treated with water to wash out the sulphate of alumina formed. This salt forms, on cooling, a mass of interlaced crystals, being the sulphate of alumina already described, $Al_2O_3.3SO_3+18HO$. Some clays and aluminous schists do not require to be heated before being treated with sulphuric acid. The addition of sulphate of potassa converts the last salt into alum.

The old mode of making alum is still largely practised in England. A series of beds occur low in many of the coal measures, which contain much bisulphide of iron. One of these, known as alum-slate, is a silicious clay, containing a considerable portion of coaly matter, and of the metallic sulphide in a state of minute division. When this mineral is exposed to air and moisture, it soon exfoliates, from the formation of sulphate of iron, the bisulphide of iron absorbing oxygen like a pyrophorus. The excess of sulphuric acid formed attacks the other bases present, of which the most considerable is alumina. Aluminous schists often require to be moderately calcined or roasted before they undergo this change in the atmosphere. The mineral being lixiviated, after a sufficient exposure, affords a solution of sulphate of alumina and protosulphate of iron, from which the latter salt is first separated by crystallization. The subsequent addition of sulphate of potassa to the liquor causes the formation of alum; the chloride of potassium answers the same purpose, and has the advantage over the sulphate that it converts the remaining sulphates of iron into chlorides, which are very soluble, and from which the alum is most easily separated by crystallization. A very pure alum is also obtained in the Roman states from *alum-stone,* which is simply heated till sulphurous acid begins to escape from it, and the residue of this calcination treated with water. This mineral contains an insoluble subsulphate of alumina with sulphate of potassa. The heating has the effect of separating the excess of alumina, so that a neutral sulphate of alumina is formed. Alum-stone appears to be continually produced at the Solfatara, near Naples, and other volcanic districts, by the joint action of sulphurous acid and oxygen upon trachyte, a volcanic rock composed almost entirely of felspar. [*See Supplement,* p. 820.]

The solubility of crystallized alum, according to M. Poggiale, is as follows:—

100 parts of water at 32° (0° C.) dissolve 3.29 parts of alum.
— at 50° (10° C.) — 9.52 —
— at 86° (30° C.) — 22.00 —
— at 140° (60° C.) — 31.00 —
— at 158° (70° C.) — 90.00 —
— at 212° (100° C.) — 357.00 —

It crystallizes very readily in regular octohedrons, of which the apices are always more or less truncated, from the appearance of faces of the cube; their density is 1.71. The taste of alum is sweet and astringent, and its action decidedly acid; it dissolves metals, with evolution of hydrogen, as readily as free sulphuric acid. The crystals effloresce slightly in air, and, when heated, melt in their water of crystallization, which amounts to 45.5 per cent. of their weight, or 24 equivalents. The fused salt, in losing this water, becomes viscid, froths greatly, and forms a light porous mass, known as burnt alum. When submitted to a graduated temperature, alum loses 10 equivalents of water at 212°, and 9 equivalents more at 248° (120° C.); leaving alum combined with 5 eq. of water. This last substance can support a temperature of 320° (160° C.) without losing more water. At 356° (180° C.) it loses 4 equivalents of water; a salt then remains which parts with ½ eq. of water at 392° (200° C.), leaving alum in combination with ½ eq. of water (Hertwig).

A pyrophorus is formed from an intimate mixture of 3 parts of alum and 1 of sugar, which are first evaporated to dryness together, and then introduced into a small stoneware-bottle, and this placed in a crucible and surrounded with sand. The whole is heated to redness till a blue flame appears at the mouth of the bottle, which is allowed to burn for a few minutes, and the mouth then closed by a stopper of chalk. After cooling, the bottle is found to contain a black powder, which becomes red-hot when exposed to air, and catches fire also and burns with peculiar vivacity in oxygen-gas. This property appears to depend upon the highly divided state of sulphide of potassium, which is intermixed with charcoal and sulphate of alumina. A pyrophorus can be produced from sulphate of potassa alone, without the sulphate of alumina; but it does not so certainly succeed.

If the quantity of carbonate of soda necessary to neutralize a portion of alum be divided into three equal portions, and added in a gradual manner to the aluminous solution, it will be found that the alumina at first precipitated is re-dissolved upon stirring, and that no permanent precipitate is produced till nearly two parts of alkaline carbonate are added. It is in the condition of this partially neutralized solution that alum is generally applied as a mordant to cloth. Animal charcoal readily withdraws the excess of alumina from this solution, and so does vegetable fibre, probably from a similar attraction of surface. When this solution is concentrated by evaporation, alum crystallizes from it, generally in the cubic form, and the excess of alumina is precipitated.

Basic alum is a granular crystalline compound, which precipitates when gelatinous alumina is boiled in a solution of alum. The formula of this salt is $HO.SO_3 + 3(Al_2O_3.SO_3) + 9HO$: the alum-stone used in preparing the Roman alum has the same composition.

Sulphate of ammonia may be substituted for sulphate of potassa in alum, giving rise to *ammoniacal alum*,

$$NH_4O.SO_3 + Al_2O_3.3SO_3. + 24HO.,$$

which agrees very closely in properties with potassa-alum.

Sulphate of alumina also combines with sulphate of soda, forming *soda-alum*, which crystallizes in the same form as common alum, and also contains 24HO, the formula of soda-alum being,

$$NaO.SO_3 + Al_2O_3.3SO_3 + 24HO.$$

Crystals are obtained by mixing the sulphates of soda and alumina, and leaving a concentrated solution to spontaneous evaporation; or by pouring spirits of wine upon the surface of such a solution contained in a bottle, which deposits crystals as the alcohol gradually diffuses through it. This salt effloresces in air as rapidly as sulphate of soda. It is very soluble in water, 10 parts of water at 60° dissolving 11 parts of this salt.

Sulphate of alumina also combines with the sulphate of protoxide of iron, when dissolved with that salt and a considerable admixture of sulphuric acid (Klauer). The double salt was found to contain 1 eq. of protosulphate of iron ($FeO.SO_3$), 1 eq of sulphate of alumina ($Al_2O_3.3SO_3$), and 24 eq. of water ($24HO$), which indicates a similarity in composition to alum. But it is deposited in long acicular crystals, which do not belong to the octohedral system, and has therefore no claim to be considered an alum. A similar salt with magnesia was obtained in the same way. Another combination of the same class, containing the sulphate of manganese, forms a white fibrous mineral found in a cave upon Bushman's river in South Africa. This native sulphate of alumina and manganese has been carefully examined by Dr. Apjohn and by Sir R. Kane, and found to contain $25HO$. It is probable that if the proportion of water in Klauer's salts were accurately determined, it would be found to be the same. These salts may be represented as compounds of a magnesian sulphate, retaining its single equivalent of constitutional water, with sulphate of alumina; the manganese compound thus: —

$$MnO.SO_3.HO+Al_2O_3.3SO_3+24HO.$$

Certain salts have been formed, isomorphous with alum, and strictly analogous in composition, in which the alumina is replaced by metallic oxides isomorphous with it, namely, by sesquioxide of iron, sesquioxide of manganese, and sesquioxide of chromium. To these salts the generic term alum is applied, and the species is distinguished by the name of the metallic sesquioxide it contains; as *iron-alum, manganese-alum,* and *chrome-alum.*

Alumina dissolves freely in most acids, but, like metallic peroxides in general, it affords few crystalline salts, except double salts. The oxalate of potassa and alumina is the only other of these that has been fully examined. It is remakable for its composition, containing 3 eq. of oxalate of potassa to 1 eq. of oxalate of alumina, with 6 eq. of water. Its formula is, therefore,

$$3(KO.C_2O_3)+Al_2O_3.3C_2O_3+6HO.$$

Like alum it is the type of a genus of double salts. The corresponding oxalates, containing soda, crystallize with $10HO$. — (Phil. Trans. 1837, p. 54.)

Nitrate of alumina is said to crystallize with difficulty in prismatic crystals radiating from a centre. [*See Supplement*, p. 820.]

An insoluble *phosphate of alumina* precipitates when phosphate of soda is added to a solution of alum. By fusion it gives a glass, like porcelain: its composition is $2Al_2O_3.3PO_5$ (Berzelius). This salt, dissolved in an acid and precipitated by ammonia in excess, gives a more highly basic phosphate, of which the formula is $4Al_2O_3.3PO_5$ (Berzelius). The last phosphate of alumina occurs in nature, in combination with fluoride of aluminum, in the form of radiating crystals, and is named *wavellite,* of which the formula is $Al_2F_3+3(4Al_2O_3.3PO_3)+36HO$. A phosphate of alumina and lithia, containing the same subphosphate of alumina, forms the rare mineral *amblygonite,* and may be prepared artificially: its formula is $2LiO.PO_5+4Al_2O_3.3PO_5$.

SILICATES OF ALUMINA.

The varieties of *clay* are essentially silicates of alumina, but composed as they are of the insoluble matter of various rocks destroyed by the action of water, it is not to be expected that they will be uniform in composition. Mitscherlich considers it probable that the basis of clay is usually a subsilicate of alumina, of which the formula is $2Al_2O_3.3SiO_3$; and which contain 57.42 parts of silicic acid and 42.58 of alumina in 100 parts. But from the analysis of Mosander, the refractory clay of Stourbridge (a fire-clay) is a neutral silicate of alumina, $Al_2O_3.3SiO_3$. *China-clay* or *kaolin*, which is prepared from decaying granite, being the result of the decomposition of the felspar and mica of that mineral, is not uniform in its composition. The clay from a white bed of the Plastic Clay formation, which is worked for the purposes of pottery in the neighbourhood of Farnham, gave Mr. Way the following results:—

White clay dried at 212° contained in 100 parts—

Insoluble in acids, 58.03	Silicic acid	42.28
	Alumina	11.45
	Oxide of iron	3.53
	Lime	0.55
	Magnesia	0.22
Soluble in acids, 41.97	Silicic acid	18.73
	Alumina	12.15
	Oxide of iron	2.11
	Lime	0.27
	Magnesia	0.29
	Potassa	0.86
	Soda	1.41
	Water of combination	6.15
		100.00

Clay, and soils in general from the clay which they contain, possess a remarkable power of separating salts of ammonia and potassa from their solutions, and retaining these bases, first observed with reference to ammonia by Mr. H. O. Thomson, and since ably investigated by Professor Way. A light soil digested with a weak solution of caustic ammonia for two hours, withdrew 0.3438 per cent. of its weight of that base, and 0.3478 per cent. of ammonia from a solution of the hydrochlorate of ammonia, the latter salt being decomposed, and chloride of calcium found in solution. The sulphate of ammonia was decomposed by the same soil and by the clay above described, in a similar manner, sulphate of lime appearing in solution. Hence, when putrid urine and other soluble manures are filtered through clay or soil, the ammonia is entirely retained, while the water drains away containing only earthy salts. This absorptive power of clay is not destroyed by boiling the clay with an acid, nor by drying it between 150° and 200°; but the property is nearly lost in thoroughly burnt clay. The lime present in clay, which appears to be necessary to this action, is not entirely withdrawn by boiling with an acid, as will be observed in the preceding analysis of clay. From the hydrochlorate of ammonia 0.2010 per cent. of ammonia was withdrawn by the white clay, and 0.4366 per cent. of potassa, from the nitrate of potassa, by the same clay. The only solutions of lime which came under the influence of this absorbing power of clay and soils were those of hydrate of lime, and of carbonate of lime in carbonic acid water. Mr. Way does not propose any rationale of this remarkable action of clay, but excludes the supposition of its being due to free alumina and silicic acid (Journal of the Royal Agricultural Society of England, xi. 313, 1850).

A subsilicate of alumina exists, forming a very hard crystallized mineral, *disthene* or *cyanite*, of which the formula is $2Al_2O_3.SiO_3$.

Double silicates of alumina and potassa are extensively diffused in the mineral kingdom, forming a very considerable portion of the solid crust of the globe. The most usual of these double salts are the following:

Potash-Felspar, which is crystallized in oblique rhomboidal prisms, of density 2.5, is composed of single equivalents of the neutral silicates of potassa and alumina.

Its formula is therefore analogous to that of anhydrous alum, silicon being substituted for sulphur; $KO.SiO_3+Al_2O_3.3SiO_3$. It is one of the three principal constituents of granite and gneiss. This species of felspar is named *orthose*. Other varieties of felspar are *albite*, or soda-felspar, containing silicate of soda, $NaO.SiO_3$, in the place of silicate of potassa; lithia-felspar *(petalite, triphane)*, $LiO.SiO_3+Al_2O_3.3SiO_3$; and lime-felspar *(labradorite, anorthite)*, $CaO.SiO_3+Al_2O_3.3SiO_3$. The alkaline base of felspars is often partially replaced by lime and magnesia, and the most general formula for a felspar would be —

$$\left.\begin{matrix}KO\\NaO\\CaO\\MgO\end{matrix}\right\} SiO_3+Al_2O_3.3SiO_3.$$

Amphigen or *leucite* occurs principally in the lava of Vesuvius in a crystallized state. The relation between the potassa and alumina is the same as in orthose, but it contains one-third less silicic acid. Hence the formula $3KO.2SiO_3+3(Al_2O_3.2SiO_3)$. A similar combination is obtained by precipitating a saturated solution of alumina in potassa, by a solution of silicate of potassa (Berzelius).

When a mixture of silicic acid and alumina is fused with an excess of potassa, and the fused mass washed with water, to withdraw everything soluble, a powder remains in which the potassa and alumina are still in the ratio of single equivalents, but in which the oxygen of the silicic acid is equal to that of the bases. This double salt has consequently the formula, $3KO.SiO_3+3Al_2O_3.3SiO_3$.

Analcime is the soda silicate proportional to amphigen. It is crystallized like amphigen, but contains 6 eq. of water. Its formula is $3NaO.2SiO_3+3(Al_2O_3.2SiO_3)+6HO$.

A third compound may be prepared, corresponding with the artificial potassa-compound above. It occurs also in hexagonal prisms in the lava of Vesuvius, forming the mineral *nephelin*.

Garnet is a double basic silicate of lime and alumina, of which the formula is $3CaO_3.SiO_3+Al_2O_3.SiO_3$.

The *silicates of lime and of alumina* combine in many different proportions, forming a great variety of minerals. Most of them contain water, in consequence of which they froth when heated before the blow-pipe, and hence are called *zeolites*. One of these, named *stilbite*, from its shining lustre, corresponds in composition with felspar, but contains in addition 6 eq. of water: its formula is

$$CaO.SiO_2+Al_2O_3.3SiO_3+6HO.$$

A small portion of one or other of the alkalies is often found in these minerals, besides small quantities of protoxide of iron and other magnesian oxides, replacing, it may be presumed, the lime in part. This extensive class of minerals has been very fully studied by Dr. Thomson, who has added considerably to their number.—(Outlines of Mineralogy and Geology, vol. i.)

EARTHENWARE AND PORCELAIN.

The silicate of alumina is the basis of all the varieties of pottery. When moistened with water, clay possesses a high degree of plasticity, and can be extended into the thinnest plates, fashioned into form by the hand, by pressure in moulds, or, when dried to a certain point, be modelled on the turning lathe. It loses its water also in drying, without cracking, provided it is allowed to contract equally in all directions, and acquires greater solidity. When heated more strongly in the potter's kiln, in which it is not fused nor its particles agglutinated by partial fusion, it becomes a strong solid mass, which adheres to the tongue and absorbs water with avidity. To render it impermeable to that liquid, it is covered with a vitreous matter, which is fused at a high temperature, and forms an insoluble glaze or varnish upon its surface. But the interior mass of ordinary pottery has always an earthy fracture, and presents no visible trace of fusion.

When an addition is made to the clay, of some compound, which softens or fuses at the temperature at which the earthenware is fired, such as felspar in powder, then the clay is agglutinated by the fusible ingredient, and the mass is rendered semi-transparent, in the same manner as paper that has imbibed melted wax remains translucent after the latter has fixed. The accidental presence of lime, potassa, protoxide of iron, or any similar base in the clay, may produce the same effect by forming a fusible silicate diffused through the clay in excess. Such is the constitution of porcelain, and of brown salt-glaze ware of which stoneware bottles are made, which is indeed a sort of porcelain. When these kinds of ware are covered by a fusible material, similar to that which has entered into the composition of their body, and a second time fired, they acquire a vitreous coating. Their fracture is vitreous and not earthy, the broken surface does not adhere to the tongue, and the mass has much greater solidity and strength than the former kinds of earthenware. In combining the ingredients of porcelain, an excess of the fusible material is to be avoided, as it may cause the vessels to soften so much in the kiln as to lose their shape, or even to run down into a glass; while on the other hand if the vitrifiable constituent is in too small a proportion, the heat of the furnace may be inadequate to soften the mass, and to agglutinate it completely.

Felspar mixed with a little clay is used as the glaze for the celebrated porcelain of Levres. Elsewhere a mixture of sulphate of lime, ground porcelain and flint, is sometimes used as a glaze. In painting porcelain, the same metallic oxides are employed as in staining glass. They are combined with a vitrifiable material, generally made thin with oil of turpentine, and applied to the pottery, sometimes under and sometimes above the glaze. To fuse the latter colours, the porcelain must be exposed a third time to heat, in the enamel furnace.

Stoneware. — The principal varieties of clay used here, according to Mr. Brande, are the following: — 1. *Marly clay*, which, with silicic acid and alumina, contains a portion of carbonate of lime: it is much used in making pale bricks, and as a manure, and when highly heated enters into fusion. 2. *Pipe-clay*, which is very plastic and tenacious, and requires a higher temperature than the preceding for fusion: when burned it is of a cream colour, and is used for tobacco-pipes and white pottery. 3. *Potters' clay* is of a reddish or grey colour, and becomes red when heated; it fuses at a bright-red heat; mixed with sand it is manufactured into red bricks and tiles, and is also used for coarse pottery (Manual of Chemistry, p. 1131). The glaze is applied to articles of ordinary pottery after they are fired, and in the condition of biscuit-ware. They are dipped into a mixture of about 60 parts of red lead, 10 of clay, and 20 of ground flint diffused in water to a creamy consistence, and when taken out enough adheres to the piece to give a uniform glazing when again heated. To cover the red colour which iron gives to the common clays when burnt, the body of the ware is sometimes coloured uniformly of a dull green, by an admixture of oxide of chromium, or made black by oxides of manganese and iron; or oxide of tin is added to the materials of the glaze, to render it white and opaque. The patterns on ordinary earthenware are generally first printed upon tissue-paper, in an oily composition, from an engraved plate of copper, and afterwards transferred by applying the paper to the surface of the biscuit ware, to which the colour adheres. The paper is afterwards removed by a wet sponge. The fusion of the colouring matters takes place with that of the glaze, which is subsequently applied, in the second firing. The prevailing colours of these patterns are blue from oxide of cobalt, green from oxide of chromium, and pink from that compound of oxide of tin, lime, and a small quantity of oxide of chromium, known as *pink colour*.

SECTION II.

GLUCINUM, YTTRIUM, THORIUM, ZIRZONIUM

GLUCINUM.

Eq. 6.97 *or* 87.06; Gl.

Syn. Beryllium. — The compounds of this metal have a considerable analogy to those of aluminum. Glucinum is obtained from its chloride, which is decomposed by potassium in the same manner as the chloride of aluminum. This metal is fusible with great difficulty, not oxidable by air or water at the usual temperature, but it takes fire, in oxygen, at a red-heat, and burns with a vivid light. It derives its name from γλυκὺς, sweet, in allusion to the sweet taste of the salts of its oxide, glucina.

Glucina, Beryllia; Gl_2O_3 is a comparatively rare earth, but contained to the extent of 13⅔ per cent. in the emerald and beryl, of which specimens that are not transparent and well crystallized can be procured in considerable quantity. To decompose this mineral, which is a silicate of glucina and alumina, it must be reduced to an extremely fine powder, the grosser particles which fall first when the powder is suspended in water, being submitted again to pulverization, and the powder calcined with 3 times its weight of hydrate of potassa. The calcined mass is moistened with water, and then treated with hydrochloric acid, added in small portions till it is in excess. The potassa, alumina, and glucina, are thus converted into chlorides, and dissolved. The solution is evaporated to dryness on a water-bath, and the residue acidulated by a few drops of hydrochloric acid: the silicic acid remains undissolved. On adding afterwards carbonate of ammonia in considerable excess to the filtered liquid, the alumina is precipitated together with the lime and oxides of iron and chromium which are usually present, while the glucina alone remains in solution. The liquor is filtered, and the carbonate of ammonia being then expelled from it by ebullition, carbonate of glucina precipitates. The earthy carbonate is ignited, and leaves glucina in the state of a white and light powder, tasteless, infusible by heat, insoluble in water and caustic ammonia, but soluble in caustic potassa and soda. Its density is nearly 3. It is distinguished from alumina, which it greatly resembles, by absorbing carbonic acid from the air, and readily forming a carbonate; and most remarkably by being soluble, when freshly precipitated, in a cold solution of carbonate of ammonia. It is capable of decomposing the salts of ammonia in a hot solution, and replaces that base. The salts of glucina do not form an alum when treated with sulphate of potassa; nor do they become blue, like the salts of alumina, when heated before the blow-pipe with nitrate of cobalt.

Glucina combines with sulphuric acid in several proportions, forming a bisulphate, $Gl_2O_3 . 6SO_3$, which is crystallizable; a neutral sulphate, $Gl_2O_3 . 3SO_3 + 12HO$, which forms fine crystals; a soluble subsalt, $Gl_2O_3 . 2SO_3$, and an insoluble subsalt, $Gl_2O_3 . SO_3$.

Emerald or *beryl* is a double silicate of glucina and alumina, of the composition expressed by $Gl_2O_3 . SiO_3 + Al_2O_3 . SiO_3$; but contains besides, lime and some chromium and iron. This mineral crystallizes in six-sided prisms, which are very hard. When coloured green by oxide of chromium it forms the true emerald, and when colourless and transparent *aqua marina*, which are both ranked among the precious stones. The density of the emerald is 2.58 to 2.732.

Euclase is also a silicate of glucina and alumina. It is a very rare mineral, which crystallizes in limpid, greenish prisms.

Chrysoberyl, one of the finest of the gems, consists essentially of 1 equivalent of glucina combined with 6 equivalents of alumina, Gl_2O_3, $6Al_2O_3$.

It is very doubtful whether glucina is a sesquioxide, Gl_2O_3, analogous in composition to alumina. It is indeed quite as probable that glucina is a protoxide, GlO, analogous to magnesia. The equivalent of glucinum would then be reduced to 4.64 on the hydrogen-scale, and 58.04 on the oxygen-scale.

[*See Supplement*, p. 821.]

YTTRIUM, ERBIUM, AND TERBIUM.

Eq. 32.20 *or* 402.5; Y.

The earth yttria was discovered in 1794, by Gadolin, in a mineral from Ytterby in Sweden, which is now called gadolinite. It has since been found in several other minerals, but all of which are exceedingly rare. The metal was isolated from its chloride by Wöhler, precisely in the same manner as the two preceding metals. It is of a darker colour than these metals, and in oxidability resembles glucinum.

Yttria is considered a protoxide, YO. Its density is even greater than baryta, being 4.842. It is absolutely insoluble in the caustic alkalies, is precipitated by yellow prussiate of potassa, and its sulphate and some others of its salts have an amethystine tint, properties which distinguish it from the preceding earths. The nitrate of yttria is colourless and crystallizable. The chloride of yttrium is deliquescent, and does not appear to be volatile.

In what has hitherto been distinguished as yttria two new bases have lately been discovered by M. Mosander, which have been named *erbia* and *terbia.* These oxides are less soluble in dilute sulphuric acid than yttria, and are thereby separated from that earth. From a solution in nitric acid of the two new earths, oxide of erbium is precipitated by saturating the liquid with sulphate of potassa, in the form of a sparingly soluble double salt, while the oxide of terbium remains in solution. Each of these bases may then be precipitated singly by means of potassa.

The sulphate and nitrate of terbia readily crystallize; the former salt is efflorescent. The salts of terbia are apt on dessiccation to assume a red amethystine tint.

Erbia assumes a deep-yellow tint when made anhydrous, which appears to be due to oxidation, as the earth becomes colourless in a stream of hydrogen. The sulphate of erbia, which is crystallizable and colourless, does not effloresce in air, like the sulphate of terbia.

THORIUM, OR THORINUM.

Eq. 59.59 *or* 744.9; Th.

This element was discovered by Berzelius, in 1824, in a black mineral, like obsidian, since called *thorite*, from the coast of the North Sea. This mineral contains 57 per cent. of the thorina. This element has been named from the Scandinavian deity Thor. The metal was obtained from the chloride, and exhibited a general resemblance to aluminum. Like yttrium, it burns in oxygen with a degree of brilliancy which is quite extraordinary: the resulting oxide does not exhibit the slightest trace of fusion.

Thorina is considered a protoxide, ThO. Its density is 9.402, and therefore superior to that of all other earths. Thorina forms a hydrate, ThO.HO, which is soluble in alkaline carbonates and in all the acids. It resembles yttria in being insoluble in the caustic alkalies, but differs from that earth in the peculiar property of its sulphate, to be precipitated by ebullition, and to redissolve entirely, although in a slow manner, in cold water. Its sulphate also forms a double salt with sulphate of potassa, which dissolves in water, but is insoluble in a liquid saturated with sulphate of potassa. The solutions of thorina are precipitated white by the ferrocyanide of potassium, a property by which thorina is distinguished from zirconia. Thorina is also precipitated from solutions to which an excess of acid has been added, on afterwards introducing sufficient ammonia, by which it is distinguished from magnesia.

ZIRCONIUM.

Eq. 33.62 *or* 420.2; Zr.

Zirconium is obtained by heating the double fluoride of zirconium and potassium, with potassium, in a glass or iron tube. On throwing the cooled mass into water, the zirconium remains in the form of a black powder, very like charcoal. It contains an admixture of hydrate of zirconia, which may be withdrawn from it by digestion in hydrochloric acid, at 104° (40° C.) The zirconium is afterwards washed with sal-ammoniac to remove completely chloride of zirconium, and then with alcohol to withdraw the sal-ammoniac. If washed with pure water, it is apt to pass through the filter. After being thus treated, the powder assumes, under the burnisher, the lustre of iron, and is compressed into scales which resemble graphite. When heated in air it takes fire below redness. It is very slightly attacked by either alkalies or acids, with the exception of hydrofluoric acid, which dissolves zirconium with evolution of hydrogen.

The constitution of *zirconia* is not certainly known, but it is believed to be analogous to that of alumina, Zr_2O_3. It was first recognized as a peculiar earth by Klaproth in 1789, who discovered it in the zircon of Ceylon, a silicate of zirconia; which is also found in the syenitic mountains of the south-east side of Norway. The *hyacinth* is the same mineral, of a red-colour; it is found in volcanic sand at Expailly in France, in Ceylon, and some other localities. The earth is obtained from this mineral, which is more difficult of decomposition than most others, by processes for which I must refer to Berzelius.[1]

Zirconia is a white earth, like alumina in appearance, of density 4.3. Its hydrate, after being boiled, is soluble with difficulty in acids. When heated, it parts with its water, afterwards glows strongly, from a discharge of heat, becomes denser, and less susceptible of being acted on by reagents. Zirconia forms a carbonate. When once separated from its combinations, it is insoluble in carbonate of potassa or soda, but dissolves in them in the nascent state. The salts of zirconia have a purely astringent taste. It agrees with thorina in being precipitated, when any of its neutral salts are boiled with a solution of sulphate of potassa. The chloride of zirconium is volatile, but less so than the chloride of silicium; a property which has been taken advantage of by M. Wöhler in preparing zirconia.

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[1] Traité de Chimie, ii. 171. Paris, 1846.

ORDER IV.

METALS PROPER HAVING PROTOXIDES ISOMORPHOUS WITH MAGNESIA.

SECTION I.

MANGANESE.

Eq. 27·67 *or* 345·9; Mn.

This element is found in the ashes of plants, in the bones of animals, and in many minerals, of which that employed in the preparation of oxygen is one of the richest. The black oxide of manganese was long known as *magnesia nigra*, from a fancied relation to magnesia alba; but was first thoroughly studied by Scheele, in 1774, and immediately afterwards by Gahn, who obtained from it the metal now called manganese.

From its strong affinity for oxygen, and the very high temperature which it requires for fusion, manganese is one of the most difficult of all the metals proper, to reduce and fuse into a button. Hydrogen and charcoal, at a red heat, reduce the superior oxides of this metal to the state of protoxide, without eliminating the pure metal at that temperature; but at a white heat, charcoal deprives the metal of the whole of its oxygen. The following process is recommended by M. John for the reduction of manganese: it illustrates the chief points to be attended to in the reduction of the less tractable metals. Instead of a native oxide, an artificial oxide of manganese, obtained by calcining the carbonate in a well-closed vessel, is operated upon. This oxide, which is preferred from being in a high state of division, is mixed with oil and ignited in a covered crucible, so as to convert the oil into charcoal. After several repetitions of this treatment, the carbonaceous mass is reduced to powder, and made into a firm paste by kneading it with a little oil. Finally, this paste is introduced into a crucible lined with charcoal (creuset brasqué), the unoccupied portion of which is filled up with charcoal powder. The crucible is first heated merely to redness for half an hour, to dry the mass and decompose the oil; after which its cover is carefully luted down, and it is exposed for an hour and a half to the most violent heat of a wind-furnace that the crucible itself can support without undergoing fusion. The metal is obtained in the form of a semi-globular mass or button in the lower part of the crucible, but not quite pure, as it contains traces of carbon and silicon derived from the ashes of the charcoal. By igniting the metal a second time in a charcoal crucible, with a portion of borax, John obtained it more fusible and brilliant, and so free from charcoal, that it left no black powder when dissolved in an acid.

Manganese is a greyish white metal, having the appearance of hard cast iron. Its density, according to John, is 8·013; while M. Berthier finds it to be 7·05, and Bergmann made it 6·850: according to Hjelm, it is 7·0. From its close resemblance to iron, manganese may be expected to be susceptible of magnetism; but its magnetic powers are doubtful. Péclet has endeavoured to show that manganese can assume and preserve magnetic polarity from the temperature — 4° up to 70°, but loses it again at higher temperatures. The small difference between the atomic weights of iron, manganese, cobalt, and nickel, which are respectively 28, 27·67, 29·52, and 29·57, is remarkable, attended as it is by a great analogy between these metals in many other respects.

Manganese oxidates readily in air, soon falling down as a black powder; in water it occasions a disengagement of hydrogen gas. It is best preserved in naphtha, like potassium, or over mercury. Manganese exhibits five degrees of oxidation, with two intermediate or compound oxides.

OXIDES OF MANGANESE.

Protoxide or manganous oxide	MnO.
Sesquioxide or manganic oxide	Mn_2O_3.
Bioxide or Peroxide	MnO_2.
Manganoso-manganic oxide or red oxide	Mn_3O_4, or $MnO + Mn_2O_3$.
Varvicite	Mn_4O_7, or $Mn_2O_3 + 2MnO_2$.
Manganic acid	MnO_3.
Permanganic acid	Mn_2O_7.

Protoxide of manganese: Manganous oxide; MnO, 35·67 *or* 445·9.—This is the oxide existing in the ordinary salts of manganese, which are isomorphous with the salts of magnesia. It may be obtained by fusing at a red heat in a platinum crucible, a mixture of equal parts of pure chloride of manganese and carbonate of soda, with a small quantity of sal ammoniac. By the reaction between the first-mentioned salts, chloride of sodium is produced, together with the carbonate of manganese, which is decomposed at a red heat, leaving the protoxide of that metal. The hydrogen of the sal-ammoniac at the same time reduces to the state of protoxide any bioxide which may be formed by absorption of oxygen from the air. Any one of the superior oxides of manganese, in the state of fine powder, may be converted into protoxide by passing hydrogen gas over it, in a porcelain tube at a red heat: the bioxide obtained by igniting the nitrate of the protoxide of manganese was recommended by Dr. Turner as the most easily deoxidated.

Protoxide of manganese is a powder of a greyish green colour, more or less deep. When obtained by means of hydrogen at a low temperature, it absorbs oxygen from the air, soon becoming brown throughout its whole mass, and is, indeed, sometimes a pyrophorus; but when prepared by hydrogen at a high temperature, it acquires more cohesion, and is permanent.

Protoxide of manganese dissolves readily in acids, and is a strong base. Its salts are of a pale rose tint, which is not destroyed by sulphurous or hydrosulphuric acid, and must be considered as a peculiar character of manganous salts. When the solution is colourless, as it sometimes is, the fact is explained, according to M. Görgeu, by the presence of a salt of iron, nickel, or copper; the green or blue tint of the latter metals producing white or a scarcely perceptible violet shade when combined with the rose tint of a salt of manganese. *Caustic alkalies* added to solutions of manganous salts throw down the protoxide of manganese in the form of a white hydrate, which soon absorbs oxygen from the air and becomes brown; when collected on a filter and washed, it ultimately changes into a blackish brown powder, which is the hydrate of the sesquioxide. A similar change is instantaneously produced by the action of chlorine-water upon the white hydrate, or by the addition of chloride of lime to a salt of the protoxide of manganese; but then the hydrated bioxide is formed. Protoxide of manganese resembles magnesia and protoxide of iron, in being but partially precipitated by ammonia. The *alkaline monocarbonates* precipitate white carbonate of manganese, which does not turn brown in the air, and dissolves sparingly in a cold solution of sal-ammoniac. *Bicarbonate of potash* precipitates a strong solution immediately, and renders a dilute solution slightly turbid; but if the solution contains a free acid, so that an excess of carbonic acid is set free, no precipitate is formed. The earthy carbonates do not precipitate manganous salts. *Hydrosulphuric acid* forms no precipitate in neutral solutions of manganous salts containing any of the stronger acids. In a neutral solution of the acetate, a flesh-coloured precipitate is formed after some time; but not if the solution contains free acetic acid. *Sulphide of ammo-*

nium forms in neutral solutions of manganous salts a flesh-coloured precipitate of hydrated sulphide of manganese, insoluble in excess of sulphide of ammonium, but readily soluble in acids. When exposed to the air, it turns brown on the surface, from oxidation. The least trace of iron or cobalt colours it black. *Ferrocyanide of potassium* forms in neutral solutions of manganous salts a white precipitate, having a tinge of red, and soluble in free acids. *Ferricyanide of potassium* forms a reddish precipitate, which is insoluble in acids. Manganous salts, and indeed all compounds of manganese, heated with *borax* or *phosphorus-salt* in the outer blowpipe flame, form an amethyst-coloured bead containing manganoso-manganic oxide, which becomes colourless in the inner flame by reduction of that oxide to the protoxide. This character distinguishes manganese from all other metals. The minutest trace of manganese is discovered by heating the solution with a little *bioxide of lead* and *nitric acid*, when a red tint appears due to the formation of permanganic acid (W. Crum). An equally delicate reaction is obtained in the dry way by heating the substance supposed to contain manganese with *carbonate of soda* on platinum foil in the outer blowpipe flame. The smallest trace of manganese is indicated by the formation of green manganate of soda. The delicacy of the reaction may be increased by adding a little nitre to the carbonate of soda.

Protosulphide of manganese may be procured in the dry way, by heating a mixture of bioxide of manganese and sulphur. Sulphurous acid is disengaged, and a green powder remains, which dissolves in acids with disengagement of hydrosulphuric acid. The same compound is obtained in the humid way, when acetate of manganese is decomposed by hydrosulphuric acid, or any manganous salt precipitated by an alkaline sulphide. Protosulphate of manganese, decomposed by hydrogen at a red heat, yields an oxisulphide. A crystalline sulphide is obtained by passing the vapour of bisulphide of carbon over hydrated manganic oxide ignited in a porcelain tube: the crystals are iron-black rhombic prisms, having a tinge of green, and yielding a dingy green powder (Völker).

Phosphide of manganese is obtained by exposing an intimate mixture of 10 parts of pure ignited bioxide of manganese, 10 parts of white burnt-bones, 5 parts of white quartz-sand, and 3 parts of ignited lamp-black for an hour in a closed Hessian crucible to a heat sufficient to melt cast-iron,—or by strongly igniting 10 parts of ignited phosphate of manganese, 3 parts of ignited lamp-black, and 2 parts of calcined borax in a crucible lined with charcoal. The product is a very brittle, crystalline regulus of the colour of grey cast-iron, and of specific gravity 5·951. It is permanent in the air, glows when heated in contact with air, and burns with an intense light when heated with nitre. It appears to contain Mn_5P, and is probably a mixture of Mn_3P and Mn_7P, the latter of which compounds is left behind when the substance is treated with hydrochloric acid, while the former dissolves, with evolution of non-spontaneously inflammable phosphuretted hydrogen (Wöhler).

Protochloride of manganese: $MnCl + 4HO$; $63{\cdot}17 + 36$ *or* $789{\cdot}63 + 450$.—This salt crystallizes in thick tables, which are oblong and quadrilateral, and of a rose colour; it is very soluble in water, and slightly deliquescent. The residuary liquid obtained in preparing chlorine by dissolving bioxide of manganese in hydrochloric acid, consists of chloride of manganese contaminated with a portion of sesquichloride of iron. To remove the latter and obtain a pure chloride of manganese, the solution should be boiled down considerably to expel the excess of acid, diluted afterwards with water, and boiled again with carbonate of manganese, which salt precipitates the whole of the sesquioxide of iron, forming chloride of manganese with its acid (Everitt). If about one-fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of soda, a quantity of carbonate of manganese will be obtained sufficient to precipitate the iron from the other three-fourths of the liquid, and applicable to that purpose after it has been washed. The iron may likewise be separated by evaporating the solution of the impure chloride to dryness, heating the residue to low redness in a crucible, as long as hydrochloric acid continues to escape; then leaving it to cool, exhausting with boiling water, and filtering. The hydrated chloride of iron is resolved by the heat into hydrochloric acid and sesquioxide, while the chloride of manganese remains unaltered, and is easily dissolved out by water, all the iron remaining behind. Chloride of manganese, when free from iron, is precipitated white, without any shade of blue, by ferrocyanide of potassium. The crystals retain one of their four equivalents of water at 212° (Brandes), but may be rendered anhydrous at a higher temperature. Brandes finds 100 parts of water to dissolve at 50°, 38·3; at 88°, 46·2; at 144·5°, 55 parts of the anhydrous salt. A higher temperature, instead of increasing the solubility of this salt, diminishes it. From the aqueous solution, chlorine, with the aid of heat, throws down the black hydrated bioxide of manganese. Hypochlorous acid produces a similar result, with evolution of free chlorine. Absolute alcohol dissolves half its weight of the anhydrous chloride of manganese, and affords, by evaporation in vacuo, a crystalline alcoate, containing two equivalents of alcohol.

Chloride of manganese forms two crystalline double salts with chloride of ammonium. One of these, $MnCl.\ NH_4Cl$, forms cubical crystals, containing 1 equiv. water, according to Rammelsberg, and 2 eq. according to Hauer. These crystals when ignited leave manganoso-manganic oxide in microscopic pyramids resembling Hausmanite. The other salt, $2MnCl.NH^4Cl + 4HO$, forms crystals belonging to the oblique prismatic system (Hautz). Solution of chloride of manganese containing chloride of ammonium, yields, on addition of ammonia and exposure to the air, a precipitate of hydrated manganoso-manganic oxide (Otto).

Protocyanide of manganese is obtained in the form of a yellowish or reddish-white precipitate, on adding cyanide of potassium to the solution of a manganous salt. It quickly turns brown on exposure to the air. It is decomposed by the stronger acids, and dissolves in alkaline cyanides.

The corresponding *fluoride of manganese* forms, with fluoride of silicon, a double salt which is very soluble in water and crystallizes in long regular prisms of six sides. The formula of this double salt is, according to Berzelius, $2SiF_3 + 3MnF + 21HO$.

Carbonate of manganese is a white insoluble powder, which acquires a brown tint when exposed in the dry state at 140°. It is decomposed by a red heat. Carbonate of manganese occurs in the mineral kingdom, in the form of *manganese-spar*, but never in a state of purity, being mixed with the carbonates of lime and iron, which have the same crystalline form, viz. the rhombohedral. Its presence in spathic carbonate of iron is said to be the cause why the latter yields an iron peculiarly adapted for the manufacture of steel.

Protosulphate of manganese; Manganous sulphate; $MnO,\ SO_3 + 7HO$. — A solution of this salt, used in dyeing and entirely free from iron, is prepared by igniting bioxide of manganese mixed with about one-tenth of its weight of pounded coal in a gas retort. The protoxide thus formed is dissolved in sulphuric acid, with the addition of a little hydrochloric acid towards the end of the process; the sulphate is evaporated to dryness, and again heated to redness in the gas retort. The iron is found after ignition in the state of sesquioxide and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition, and remains soluble. The salt may also be obtained by heating bioxide of manganese, previously freed from the carbonates of lime and magnesia by boiling with dilute sulphuric acid, with an equal weight of strong oil of vitriol, and gently igniting the resulting mass for an hour, to decompose the sulphates of iron and copper formed at the same time. The manganous sulphate, which remains unaltered, is then dissolved in water, and the solution evaporated to the crystallizing point. The solution is of an amethystine colour, and does not crystallize readily. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it, and rapidly becomes brown in the air; or it is peroxidized at once by passing the cloth through a solution of chloride of lime. The colour thus produced is called manganese-brown.

Crystallized under 42°, the sulphate of manganese gives crystals containing 7HO, which have the same form as sulphate of iron. The crystals which form between 45° and 68°, contain 5HO, and are isomorphous with sulphate of copper. By a higher temperature, from 68° to 86°, a third set of crystals is obtained, which contain 4HO: their form is a right rhombic prism. The sulphate of iron and other sulphates also assume the same form (Mitscherlich). This salt loses 3HO at 243°, but retains 1 eq. even at 400°, like the other magnesian sulphates. M. Kuhn finds, that when a strong solution of the sulphate of manganese is mixed with sulphuric acid and evaporated by heat, a granular salt is precipitated, which contains only one equivalent of water. This sulphate also forms with sulphate of potash a double salt containing 6HO. The anhydrous salt is soluble, according to Brandes, in 2 parts of water at 59°, in 1 part at 122°; but above the latter temperature, the salt becomes less soluble. The tetra-hydrated salt dissolves in 0·883 part of water at 43·3°; in 0·79 part at 50°; in 0·82 part at 65.8; in 0·67 part at 99·5°; and in 1·079 part at 2·1°. Manganous sulphate is insoluble in absolute alcohol, but dissolves in 500 parts of spirit of the strength of 55 per cent.

Hyposulphate of manganese; $MnO . S_2O_5+6HO$. For the preparation, see p. 253.—The bioxide of manganese used in preparing it should be previously treated with nitric acid, to dissolve out the hydrated oxide, and be well washed. The salt forms rose-coloured, generally indistinct, crystals, belonging to the doubly oblique prismatic system (Marignac). The *oxalate of manganese* is a highly insoluble salt. The *acetate* is soluble in 3½ parts of cold water, and also in alcohol. Bitartrate of potash dissolves protoxide of manganese, and forms a very soluble double salt, the *tartrate of potash and manganese,* which can be obtained, although with difficulty, in regular crystals.

Sesquioxide of manganese; Manganic oxide; Mn_2O_3; 79·34 *or* 991·8.—This oxide is left of a dark brown, almost black colour, when the nitrate of the protoxide is gently ignited. It also occurs crystallized in the mineral kingdom, although rarely; its density is 4·818, and it is named *braunite* as a mineral species. The hydrate of manganic oxide is formed by the oxidation in air of manganous hydrate. Manganic hydrate also frequently occurs in nature of a black colour, both crystallized and amorphous, and is often mixed with the bioxide of manganese. It constitutes the mineral species *manganite,* of which the density is 4·3 to 4·4, and the formula Mn_2O_3, HO. This hydrate may be artificially prepared by heating finely divided bioxide of manganese with monohydrated sulphuric acid, decomposing the resulting manganic sulphate with water, and washing it thoroughly (Carius). This oxide colours glass of a red or violet tint. The common violet or purple stained glass contains manganic oxide; also the amethyst.

Manganic oxide is a base isomorphous with alumina and sesquioxide of iron. It dissolves in cold hydrochloric acid without decomposition. Concentrated sulphuric acid combines with it at a temperature a little above 212°, but does not form a solution. Dilute sulphuric acid does not dissolve it, either in the cold or when gently heated, unless manganous oxide is present, even in very small quantities, in which case a violet solution is formed; hence the commonly received statement that manganic oxide forms a red solution with sulphuric acid (Carius). At somewhat elevated temperatures, acids reduce the sesquioxide of manganese to protoxide, with evolution of oxygen.

Manganic sulphate; $Mn_2O_3 . 3 SO_3$.—Prepared by mixing finely divided bioxide of manganese (obtained by passing chlorine gas through a solution of carbonate of soda in which carbonate of manganese is suspended) with monohydrated sulphuric acid to the consistence of a pulp, and gradually heating the mixture in an oil-bath to about 276°, at which point the mass becomes dark green and more mobile. It is then drained on a plate of pumice-stone to remove the greater part of the sulphuric acid; afterwards stirred up in a warm basin with the strongest nitric acid (free from nitrous acid); again drained on pumice-stone; and this treatment repeated several times: lastly, it is dried in the oil-bath at 266°, and preserved in carefully dried tubes. — Manganic sulphate thus obtained is a dark green powder which exhibits no traces of crystallization. It may be heated to 320° without decomposition, but at higher temperatures gives off oxygen and is reduced to manganous sulphate. At ordinary temperatures it is all but insoluble in concentrated sulphuric and nitric acid; with the former it may be heated nearly to the boiling point without alteration, but, when boiled with the acid, it dissolves as manganous sulphate, with evolution of oxygen. Heated with concentrated nitric acid to 212°, it turns brown, but resumes its green colour when the acid is evaporated at the lowest possible temperature. In strong hydrochloric acid, it dissolves, like the pure sesquioxide, forming a brown solution, which when heated gives off chlorine till all the sesquioxide of manganese is reduced to protoxide. Organic substances, heated with the dry salt, decompose it with considerable violence. The salt absorbs moisture very rapidly, so that it must always be kept in sealed tubes. Small quantities of it deliquesce in a few seconds, forming a violet solution, which, however, soon becomes brown and turbid from separation of the hydrated oxide. Water decomposes the salt rapidly, especially when heated, separating the pure hydrated sesquioxide. Hence the mode of preparing the hydrate above mentioned. Sulphuric acid, somewhat diluted, decomposes manganic sulphate, converting it into a red-brown powder, which appears to be a basic salt.* Manganic sulphate forms an alum with sulphate of potash (Mitscherlich): this salt occurs native in needle-shaped crystals at Alum Point, on the Great Salt Lake in North America (L. D. Gale).

Sesquichloride of manganese (Mn_2Cl_3) is formed when the sesquioxide is dissolved in hydrochloric acid at a low temperature. The solution is yellowish brown or black, according to its degree of concentration, and is decomposed by a slight elevation of temperature, with evolution of chlorine. A corresponding *sesquifluoride* may be crystallized.

Sesquicyanide of manganese. — A compound of this cyanide is formed, when manganous acetate is mixed with hydrocyanic acid in excess, then neutralized with potash and evaporated. The manganous cyanide then absorbs oxygen, and is converted into hydrated manganic oxide and manganic cyanide, which last combines with cyanide of potassium, and appears, on the cooling of a concentrated solution, in red crystals, which dissolve easily in water (Mitscherlich). This salt is analogous to red prussiate of potash, containing manganese instead of iron, and may, therefore, be represented as containing manganicyanogen — a *manganicyanide of potassium*, $K_3(Mn_2Cy_6)$. As a double cyanide, its formula would be, $3KCy.Mn_2Cy_3$.

Red oxide of manganese, $MnO.Mn_2,O_3$, named by Berzelius manganoso-manganic oxide, is always produced when any oxide of manganese is heated strongly in air. It is a double oxide, being a compound of single equivalents of protoxide and bioxide of manganese. It forms the mineral *Hausmanite*, which differs from manganite in having manganous oxide in place of water. Its density is 4·722. Berthier finds that strong nitric acid dissolves out the protoxide of manganese from the red oxide, and leaves a remarkable hydrate of the bioxide, of which the formula is $4MnO_2+HO$.

Bioxide or Peroxide of manganese; Black oxide of manganese; MnO_2; 43·67 *or* 545·9. — This is the well-known ore of manganese employed in the preparation of oxygen and chlorine. It generally occurs massive, of an earthy appearance, and contaminated with various substances, such as sesquioxide of iron, silica, and carbonate of lime; but sometimes of a fibrous texture, consisting of small prisms

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* Carius, *Ann. Ch. Pharm.* xcviii., 53.

radiating from a common centre. Its density varies from 4·819 to 4·94; as a mineral species it has been named *pyrolucite.*[*] Another important variety of this ore, known as *wad*, is essentially a hydrate, containing, according to Dr. Turner, 1 eq. of water to 2 eq. of peroxide. A hydrated bioxide, consisting of single equivalents of its constituents, is formed by precipitating the protosalts of manganese with chloride of lime; and the same compound results from the decomposition of the acids of manganese, when diluted with water or an acid. It is possible that the equivalent of this oxide should be doubled, and that its proper formula is Mn_2O_4, corresponding with peroxide of chlorine, ClO_4.

Bioxide of manganese loses one-fourth of its oxygen at a low red heat, and is is changed into sesquioxide; at a bright red heat it loses more oxygen, and becomes red oxide, the condition into which all the oxides of manganese pass when ignited strongly in the open air. The bioxide does not unite either with acids or with alkalies. When boiled with sulphuric acid, it yields oxygen gas and a sulphate of the protoxide. In hydrochloric acid it dissolves with gentle digestion, evolving chlorine gas, and forming protochloride of manganese (page 433). It is extensively used in the arts for preparing chlorine, and also to preserve glass colourless by its oxidating action. In the last application, it is added to the vitreous materials in a relatively small proportion, and becomes protoxide, which is not a colouring oxide, while as sesquioxide it would stain glass purple. At the same time it destroys carbonaceous matter, and converts protoxide of iron, which colours glass green, into sesquioxide, which is less injurious.

The mineral *varvicite* was discovered by Mr. R. Phillips among some ores of manganese from Hartshill in Warwickshire. It is distinguished from the bioxide by being much harder, having more of a lamellated structure, and by yielding water freely when heated to redness. Its density is 4·531. It may be supposed to consist of 1 eq. of sesquioxide, and 2 eq. of bioxide with 1 eq. of water (Dr. Turner); its formula is, therefore, $Mn_2O_3 . Mn_2O_4+HO$.

VALUATION OF BIOXIDE OF MANGANESE.

The numerous applications of the higher oxides of manganese depending upon the oxygen which they can furnish, render it important to have the means of easily and expeditiously estimating their value for such purposes. The value of these oxides is exactly proportional to the quantity of chlorine which they produce when dissolved in hydrochloric acid, and the chlorine can be estimated by the quantity of protosulphate of iron which it oxidizes. Of pure bioxide of manganese 43·7 parts (1 eq.) produce 35·5 parts of chlorine, which oxidize 278 parts (2 eq.) of crystallized protosulphate of iron. Hence 50 grains of bioxide of manganese yield chlorine sufficient to oxidize 317 grains (more exactly, 316·5 grs.) of protosulphate of iron.

50 grains of the powdered oxide of manganese to be examined are weighed out, and also any known quantity, not less than 317 grains, of the sulphate of iron (copperas) employed in chlorimetry. The oxide of manganese is thrown into a flask containing an ounce and a half of strong hydrochloric acid, diluted with half an ounce of water, and a gentle heat applied. The sulphate of iron is gradually added in small quantities to the acid, so as to absorb the chlorine as it is evolved; and the addition of that salt continued, till the liquid, after being heated, gives a blue precipitate with the red prussiate of potash, and has no smell of chlorine, which are indications that the protosulphate of iron is present in excess. By weighing what remains of the sulphate of iron, the quantity added is ascertained; say *m* grains. If the whole manganese were bioxide, it would require 317 grains of sulphate of iron, and that quantity would, therefore, indicate 100 per cent. of bioxide in the specimen; but if a portion of the manganese only is

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[*] From πυρ, fire, and λυω, I wash; in allusion to its being employed to discharge the brown and green tints of glass.

bioxide, it will consume a proportionally smaller quantity of the sulphate, which quantity will give the proportion of the bioxide, by the proportion: as 317 : 100 : : m : per-centage required. The per-centage of bioxide of manganese is thus obtained by multiplying the number of grains of sulphate of iron oxidized by 0·317. It also follows that the per-centage of chlorine which the same specimen of manganese would afford, is obtained by multiplying the number of grains of sulphate of iron oxidized by 0·2588.

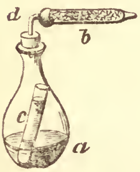
Another mode of estimation is to pass the chlorine gas, obtained by heating the manganese in a flask with hydrochloric acid, into a solution of sulphurous acid, quite free from sulphuric (it should give no precipitate with chloride of barium); the chlorine converts an equivalent quantity of sulphurous acid into sulphuric. The liquid is then mixed with chloride of barium, and boiled to expel the excess of sulphurous acid, after which the sulphate of baryta is thrown on a filter, washed, dried, ignited, and weighed. The 116·64 gr., or 1 eq. of sulphate of baryta, correspond to 43·7 gr., or 1 eq. of bioxide of manganese.

The value of commercial oxide of manganese may also be estimated by heating it with hydrochloric acid and oxalic acid. The disengaged chlorine then converts the oxalic acid into carbonic acid, — 2 eq. of carbonic acid representing 1 eq of chlorine, and therefore 1 eq. of bioxide of manganese:

$$C_2HO_4 + Cl = 2CO_2 + HCl.$$

A convenient apparatus for the determination is a small light glass flask (fig. 186), of 3 or 4 oz. capacity, having a lipped edge, and fitted with a perforated cork. A piece of tube, about 3 inches long, drawn out at one end, and filled with fragments of chloride of calcium, to absorb water, is fitted by means of a small cork and a bent tube to the mouth of the flask. A short tube closed at one end, and small enough to go into the flask, is used to contain the hydrochloric acid. Fifty grains of the mineral, in the state of very fine powder, are introduced into the flask, together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid in the tube, as shown in the figure: 50 grains of crystallized oxalic acid are then added, the chloride of calcium tube fitted on, and the whole quickly weighed. The flask is then tilted so as to allow the hydrochloric acid to flow out of the tube, and come in contact with the mixture of manganese and oxalic acid, and a gentle heat applied to determine the action. Carbonic acid is then evolved, and escapes through the chloride of calcium tube. To expel the last portions of carbonic acid, the liquid must be ultimately heated till it boils; after which it is left to cool, and weighed: the loss of weight gives the quantity of carbonic acid. Now, as 43·67, the equivalent of bioxide of manganese, is nearly double that of carbonic acid, which is 22, the loss of weight in the apparatus may be taken to represent the quantity of real bioxide in the 50 grains of the sample. [For other methods, see Appendix.]

FIG. 186.



To obtain a complete appreciation of the value of a sample of manganese, it is not sufficient to know the per-centage of real bioxide in it, — or, which comes to the same thing, the quantity of chlorine it is capable of yielding, — but we must also know the quantity of hydrochloric acid which must be consumed for evolving this chlorine. If the sample consists of pure bioxide, half the acid used will give up its chlorine; if it be pure sesquioxide, only a third of the acid will be changed into chlorine. The quantity of acid required will therefore be greater in the latter case than in the former in the ratio of 3 : 2. Lastly, if the oxide contains lime, baryta, or oxide of iron, these bases will neutralize a portion of the acid without supplying any chlorine. To determine the expenditure of acid, a known weight of the oxide is heated with a known quantity of hydrochloric acid of given strength, the chlorine being suffered to escape, but the hydrochloric acid which would otherwise escape undecomposed being collected in a small receiver moistened on the inside. When the action is over, the acid thus condensed is added to that in the flask, the whole diluted with water, and the quantity of free acid determined by adding a graduated alkaline solution, till the precipitate which forms no longer redissolves on agitation. The quantity of free acid thus determined is then to be deducted from the original quantity, and the difference gives the quantity consumed.

Manganic acid; MnO_3; 51·67 *or* 645·9.—When bioxide of manganese is strongly ignited with hydrate or carbonate of potash in excess, manganic acid is formed, under the influence of the alkali, together with a lower oxide of manganese. Ignition in open vessels, or with an admixture of nitrate of potash, increases the production of the acid, by the absorption of oxygen which then occurs. The product has long been known as *mineral chameleon,* from the property of its solution, which is green at first, to pass rapidly through several shades of colour. But a more convenient process for preparing manganate of potash is that recommended by Dr. Gregory. He mixes intimately 4 parts of bioxide of manganese in fine powder with 3½ parts of chlorate of potash, and adds them to 5 parts of hydrate of potash dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and afterwards ignited in a platinum crucible, but not fused, at a low red heat. The ignited mass, digested in a small quantity of cold water, forms a deep green solution of the alkaline manganate, which may be obtained in crystals of the same colour by evaporating the solution over sulphuric acid in the air-pump. Zwenger, by igniting bioxide of manganese with 3 parts of nitric acid, and evaporating the aqueous solution in vacuo, obtained reddish-brown crystals containing $KO.MnO_3$. On exposure to the air, they became dull and dark green. The manganates were discovered by Mitscherlich to be isomorphous with the sulphates and chromates. It has not yet been found possible to isolate manganic acid. Its salts in solution readily undergo decomposition, unless an excess of alkali is present; and are also destroyed by contact of organic matter, such as paper.

Permanganic acid, Mn_2O_7; 111·34 *or* 1391·8.—When the green solution of manganate of potash, prepared as above directed, is diluted with boiling water, hydrated bioxide of manganese subsides, and the liquid assumes a beautiful pink or violet colour. The manganic acid is resolved into bioxide of manganese and hypermanganic acid:

$$3MnO_3 = MnO_2 + Mn_2O_7.$$

The permanganate of potash should be rapidly concentrated, without contact of organic matter, and allowed to crystallize. A better process for obtaining this salt is to mix 1 part of bioxide of manganese, in very fine powder, with 1 part of chlorate of potash; introduce this mixture into a solution of 1¼ part of caustic potash in the smallest possible quantity of water; evaporate to dryness, during which process a considerable quantity of manganate of potash is formed; then heat the mixture slowly to dull redness; boil the product in water; filter through asbestos, and concentrate by evaporation: the liquid, on cooling, deposits permanganate of potash in crystals. It may be purified by solution in a small quantity of boiling water, and recrystallization. The crystals are of a dark purple colour, almost black, and soluble in sixteen times their weight of cold water; they were found by Mitscherlich to be isomorphous with perchlorate of potash; they dissolve in 16 parts of water at 60° (Regnault). The permanganates give out oxygen when heated, and are reconverted into manganates. Their solutions have a rich purple colour, and are so stable that they may be boiled, if concentrated. A small portion of a permanganate imparts a purple colour to a very large quantity of water.

When a strong solution of caustic potash is added to a dilute solution of permanganate of potash, the liquid changes colour, assuming first a violet, and afterwards an emerald-green tint. The permanganate is in fact converted into manganate, a double quantity of potash having entered into combination with the acid:

$$KO.Mn_2O_7 + KO = 2(KO.MnO_3) + O.$$

The oxygen thus liberated remains dissolved in the water. This transformation is due to the great basic power of the potash. Acids produce the contrary effect, that is to say, they convert manganates into permanganates.

The insoluble manganate of baryta may be formed by fusing bioxide of manganese with nitrate of baryta; and when mixed with a little water, and decomposed by an equivalent quantity of sulphuric acid, affords free permanganic acid. In Mitscherlich's experiments, the free acid appeared to be a body not more stable than bioxide of hydrogen, being decomposed between 86° and 104°, with escape of oxygen gas and precipitation of hydrated bioxide of manganese. It bleached powerfully, and was rapidly destroyed by all kinds of organic matter. M. Hünefeld, on the other hand, obtained permanganic acid in a state in which it could be preserved, evaporated, redissolved, &c. He washed the manganate of baryta with hot water, by which it is resolved into bioxide of manganese and permanganate of baryta, and then added to it the quantity of phosphoric acid exactly necessary to neutralize the baryta. The liberated permanganic acid was dissolved out, evaporated to dryness, and by a second solution and evaporation, obtained in the form of a reddish-brown mass, crystalline and radiated, which exhibited the lustre of indigo at some points and was entirely soluble in water. When dry permanganic acid was fused in a retort with anhydrous sulphuric acid, and afterwards distilled at a higher temperature, an acicular sublimate of a crimson red colour was obtained, which appeared to be a combination of permanganic and sulphuric acids. (Berzelius's *Traité*, i. 522.) When monohydrated sulphuric acid is poured upon a somewhat considerable quantity of crystallized permanganate of potash, the salt is decomposed with great evolution of heat, red flames bursting out, oxygen being evolved, and manganic oxide set free in dark-brown flakes and shreds like spider-lines. The red flames seem to show that permanganic acid is gaseous at the high temperature produced by the reaction. (Wöhler.)

Perchloride of manganese, Mn_2Cl_7, is a greenish yellow gas, which condenses at 0° F. into a liquid of a greenish-brown colour. This liquid diffuses purple fumes, owing to the formation of hydrochloric and permanganic acids, by the decomposition of the moisture of the air. It was formed by Dumas by dissolving manganate of potash in oil of vitriol, pouring the solution into a tubulated retort, and adding by degrees small portions of chloride of sodium or potassium, completely freed from water by fusion. The perchloride of manganese is the result of a reaction between the liberated hypermanganic and hydrochloric acids:

$$Mn_2O_7 + 7HCl = Mn_2Cl_7 + 7HO.$$

A corresponding *perfluoride of manganese* was formed by Wöhler by distilling, in a platinum retort, a mixture of manganate of potash and fluor-spar in powder, with fuming sulphuric acid. It is a greenish-yellow gas, which likewise produces purple fumes in damp air.

Isomorphous relations of manganese. — There is no other element whose compounds enter into so many isomorphous groups, and connect so large a proportion of the elements by the tie of isomorphism, as manganese. The salts of its protoxide are strictly isomorphous with the salts of magnesia and its class; so that manganese belongs to and represents the magnesian family of elements. The same metal connects the sulphur family with the magnesian, by the isomorphism of the sulphates and manganates; and, therefore, sulphur, selenium, and tellurium are thus allied to the magnesian metals. An equally interesting relation is that of permanganic with perchloric acid, and the isomorphism, which it establishes, of 2 equivalents of manganese with 1 equivalent of chlorine, and the other members of its family.

ESTIMATION OF MANGANESE, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The usual method of precipitating manganese from the solution of a manganous salt, is to add carbonate of soda at a boiling heat. The precipitated carbonate of manganese is then well washed with boiling water, and calcined at a strong red heat, whereby it is converted into manganoso-manganic oxide, Mn_3O_4, containing 72·11 per cent. of manganese. If the solution contains a considerable quantity of ammoniacal salts, it must be evaporated after mixing it with excess of carbonate of soda, and the soluble salts dissolved out of the residue by water.

Manganese is separated from the alkali-metals by means of carbonate of soda or sulphide of ammonium, which latter precipitates it in the form of sulphide. The sulphide is washed with water containing a small quantity of sulphide of ammonium; then redissolved in acid; and the manganese precipitated from the solution by carbonate of soda.

From barium and strontium, manganese is easily separated by means of sulphate of soda, which throws down the baryta and strontia as sulphates; also by sulphide of ammonium. From lime and manganese it is separated by sulphide of ammonium, which, if the solution be sufficiently dilute, precipitates the manganese alone in the form of sulphide. The separation from lime may also be effected by means of oxalate of ammonia, after the addition of chloride of ammonium to keep the manganese in solution.

From alumina and glucina, manganese, if in small or moderate quantity only, may be separated by boiling the solution with potash in an open vessel. The manganese is then precipitated in the form of sesquioxide, while the alumina and glucina are dissolved by the potash. If, however, the proportion of manganese be considerable, this method cannot be used, because the oxide of manganese carries down with it considerable quantities of alumina and glucina. In this case, the liquid must be mixed with sal-ammoniac and the alumina and glucina precipitated by ammonia. The precipitate, however, always contains small quantities of manganese, which must be separated by subsequent treatment with potash.

SECTION II.

IRON.

Eq. 28 *or* 350; Fe (*ferrum*).

The most remarkable of the metals; the production of which, from the numerous and important applications it possesses, appears to be an indispensable condition of civilization. Meteoric masses of iron, often so pure as to be malleable, are found widely although thinly scattered over the earth's surface, and probably first attracted the attention of mankind to this metal. Of the occurrence of metallic iron as a terrestrial mineral *in situ*, the best established instances are the species of native iron which accompanies the Uralian platinum, and a thin vein about two inches in thickness, observed in chlorite slate, near Canaan in the United States. In a state of combination, iron is extensively diffused, being found in small quantity in the soil, and in most minerals, and as sulphide, oxide, and carbonate, in quantities which afford an inexhaustible supply of the metal and its preparations, for economical purposes.

Iron differs from all other metals in two points, which greatly affect the methods of reducing it. Its particles agglutinate at a full red heat, although the pure metal is nearly infusible. The oxides of iron, which are easily reduced by combustible matter, thus yield in the furnace a spongy metallic mass, which may admit of being compacted by subsequent heating and hammering, if the oxide has originally been free from earthy and other foreign matter. Such probably was everywhere the earliest mode of treating the ores of iron, and we find it still followed among rude nations. But iron is also singular in forming, at an elevated temperature, a fusible compound with carbon (cast iron), the production of which facilitates the separation of the metal from every thing extraneous in the ore, and is the basis of the only method of extracting iron extensively practised.

The ore of iron most abundant in the primary formations is the black oxide or *magnetic ore*, which affords the most celebrated and valuable irons of Sweden and the north of Europe, but of which the application is greatly circumscribed from its not being associated with coal. In the secondary and tertiary formations, the anhydrous and hydrated sesquioxide of iron, *red* and *brown hematite*, occur occasionally in considerable quantity, often massive, reniform, and quite pure, at other times pulverulent and mixed with clay. It is employed to some extent in England in the last condition, but only for the purpose of mixing with the more common ore. The crystallized carbonate of iron, or *spathic iron*, is smelted in some parts of the continent, and gives an iron often remarkable for a large proportion of manganese. The celebrated iron of Elba is derived from *specular* or *oligistic iron*, a crystallized sesquioxide. But the consumption of all these ores is inconsiderable, compared with that of the *clay ironstone* of the coal measures. This is the carbonate of the protoxide of iron mixed with variable quantities of clay and carbonates of lime, magnesia, &c.; it is often called the argillaceous carbonate of iron. It is a sedimentary rock wholly without crystallization, resembling a dark-coloured limestone, but of higher density, from 2·936 to 3·471, and not effervescing so strongly in an acid. It occurs in strata, beds, or bands, as they are also named, from 2 to 10 or 14 inches in thickness, alternating with beds of coal, clay, bituminous schist, and often limestone. The proportion of iron in this ore varies considerably, but averages about 30 per cent., and after it has been calcined, to expel carbonic acid and water, about 40 per cent.*

SMELTING CLAY IRON-STONE.

The blast furnace, in which the ore is reduced, is of the form represented below, 40 to 65 feet in height, with an interior diameter of from 14 to 17 feet at the widest part. The cavity of the furnace is entirely filled with fuel and the other materials, which are continuously supplied from an opening near the top; and the combustion maintained by air thrown in at two or more openings, called tuyeres, near the bottom, under a pressure of about 6 inches of mercury, from a blowing apparatus, so as to maintain the whole contents of the furnace in a state of intense ignition. When the air to support the combustion has attained a temperature of 600° or 700°, by passing through heated iron tubes, before it is thrown into the furnace, raw coal may be used as the fuel; but with cold air, the coal must be previously charred to expel its volatile matter, and converted into coke, otherwise the heat produced by its combustion is insufficient. With the ore and fuel, a third substance is added, generally limestone, the object of which is to form a fusible compound with the earthy matter of the ore; it is, therefore, called a *flux*. Two liquid products accumulate at the bottom of the furnace, namely, a glass composed of the flux in combination with the earthy impurities

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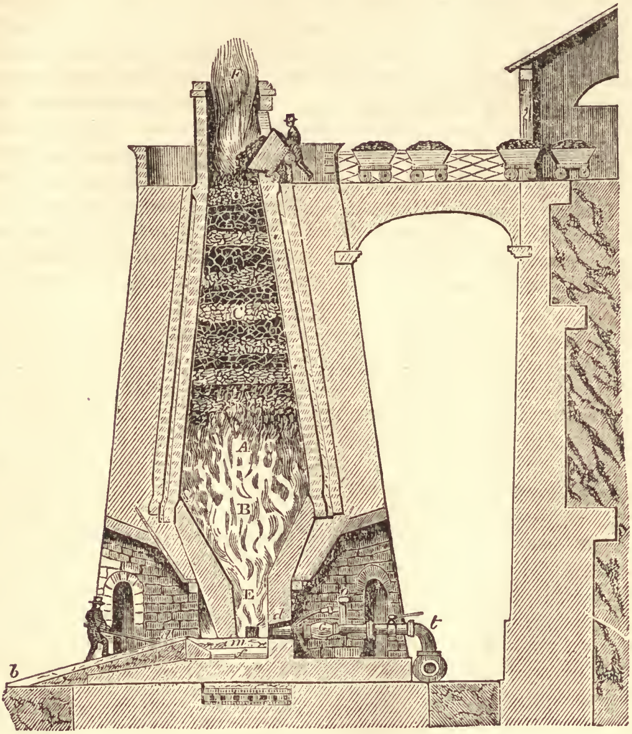
* Accurate analyses of several Scotch varieties of this ore have been published by Dr. H. Colquhoun (Brewster's *Journal*, vii. 234; or Dr. Thomson's *Outlines of Mineralogy and Geology*, i. 446); and of the French ores, by M. Berthier, in his *Traité des essais par la voie sèche*, ii. 252, a work which is invaluable for the metallurgic student, and Mitchell's *Practical Assaying*, 8vo.

of the ore, which when drawn off forms a solid *slag*, and the carbide of iron, or metal, which is the heavier of the two. It may be drawn from observations made by Dr. Clark, in 1833, on the working of the Scotch blast furnaces, under the *hot blast*, that the relative proportions of the materials, including air, and product of cast iron, are as follows:*—

Fig. 187.



	Weight.
Coal	5
Roasted iron-stone	5
Limestone	1
Air	11
Average product of cast iron	2

The ultimate fixed products are the slag and carburet of iron, but the formation of these is preceded by several interesting changes which the ore successively undergoes in the course of its descent in the furnace. A portion of the oxide of iron is certainly reduced to the metallic state, soon after its introduction, in the upper part of the furnace, by carbonic oxide and volatile combustible matter; but the reduced metal does not then fuse. A large portion of the oxide of iron must combine also, at the same time, with the silica and alumina present in the ore, which act as acids, and a glass be formed, the oxide of iron in which is scarcely reducible by carbon. But this injurious effect of the acid earths is counteracted by the lime of the flux, which, being a more powerful base than oxide of iron,

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* Edinburgh Phil. Trans. vol. 13.

liberates that oxide from the glass when the proportions of the materials introduced into the furnace are properly adjusted, and neutralizes the silica; so that the slag eventually becomes a silicate of lime and alumina, with scarcely a trace of oxide of iron. The whole oxide of iron comes thus to be exposed to the reducing action of the volatile combustible, and consequently the whole iron is probably, at one time, in the condition of pure or malleable iron. But when the metal descends somewhat farther in the furnace, it attains the high temperature at which it combines with the carbon of the coke in contact with it, and it fuses for the first time, in the form of carburet of iron. It has not yet, however, attained its ultimate condition. When it reaches, in its descent, the region of the furnace where the heat is most intense, its carbon reacts on the silica, alumina, lime, and other alkaline oxides contained in the fluid slag with which it is accompanied, reducing portions of silicon, aluminum, calcium, and other alkaline metals, which combine with the iron. The proportion of carbon replaced by silicon and metallic bases is generally found to be greater in iron prepared by the hot than by the cold blast, owing, it is presumed, to the higher temperature of the furnace with the hot blast.

The introduction of air already heated to support the combustion of the blast furnace, for which a patent was obtained by Mr. J. B. Neilson, has greatly reduced the proportion of coal required to smelt a given weight of ore, enabling the iron-master, indeed, to effect a saving of more than three-fourths of the coal where it is of a bituminous quality. The air is heated between the blowing apparatus and the furnace, by being made to circulate through a set of arched tubes of moderate diameter, heated by a fire beneath them. The air can be heated in this manner to low redness, or to near 1000°, but there is found to be no proportional advantage in raising its temperature much above the melting point of lead (612°), which is already higher than the point at which charcoal inflames. Considering the great weight of air that enters the furnace, the temperature of that material must greatly affect the whole temperature of the furnace, particularly of the lower part, where the air is admitted, and which part it is desirable should be hottest. Now a certain elevated temperature is required for the proper smelting of the ore, and, unless attained in the furnace, the fuel is consumed to no purpose. The removal of the negative influence of the low temperature of the air, appears to permit the heat to rise to the proper point, which otherwise is attained with difficulty and by a wasteful consumption of fuel. Professor Reich, of Freiberg, has observed that heating the air likewise alters the relative temperatures of different parts of the furnace, depressing in particular, and bringing nearer the tuyeres, the zone of highest temperature. The admixture of steam with the air has, he finds, precisely the opposite effect, elevating the zone of highest temperature in the furnace; so that the effect of the hot blast may be exactly neutralized by mixing steam with the hot air.

Cast iron.—The fused metal is run into channels formed in sand, and thus cast into ingots or pigs, as they are called. Cast iron is an exceedingly variable mixture of reduced substances, of which the principal is iron combined with carbon. The theoretical constitution to which that variety of it, most definite in its composition, approaches, is the following:—

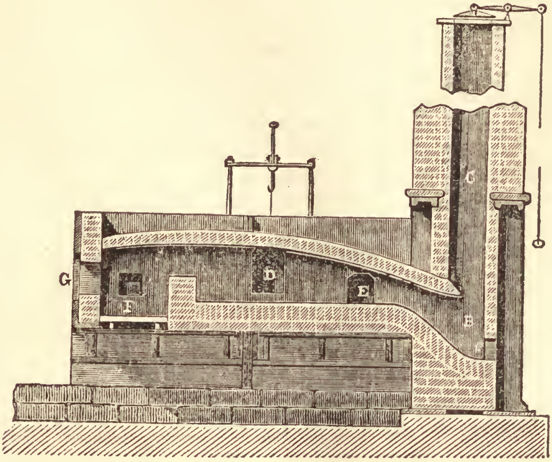
WHITE CAST IRON.

4 equivalents of iron	94·9
1 equivalent of carbon	5·1
	100·0

The difference in appearance and quality of the varieties of cast iron is not well accounted for by their composition. The grey or mottled cast iron, forming the qualities Nos. 1 and 2, presents a fracture composed of small crystals, is easily cut by the file, and is preferred for castings. It is generally supposed that a portion of uncombined carbon is diffused through the iron of these qualities, in the form of graphite. No. 3, or white cast iron, is more homogeneous; its fracture exhibits crystalline plates, like that of antimony, and is nearly white; it is exceedingly hard and brittle.

Malleable iron.—The great proportion of cast iron manufactured is afterwards refined, or converted into bar or malleable iron. The mode of effecting this conversion varies with the nature of the fuel. Where coal or coke is used, as in this country, the process consists of two stages. In the first, which is called *refining*, the pig-iron is heated in contact with the fuel in small low furnaces called *refineries*, while air is blown over its surface by means of tuyeres. The effect of this operation is to deprive the iron of a great portion of the carbon and nearly all the silicon associated with it. The metal thus far purified is run out into a trench, and suddenly cooled by pouring cold water upon it. It then forms a greyish-white very brittle mass, blistered on the surface. In this state it is called *fine metal.*

Fig. 188.



It is then ready for the second and principal operation, called the *puddling* process, which consists in heating masses of the iron with a certain access of air in a kind of reverberatory furnace, called the *puddling furnace*, of which Fig. 188 represents a vertical section. This furnace has four doors, two of which, *F* and *G*, serve for the introduction of fuel to the grate; the charge of metal is introduced at *E*; and *D* serves for the insertion of a long poker or spatula, with which the metal is stirred about. The hearth of the furnace has an aperture *B* at the back, for removing the slag. The furnace having been brought to a bright red heat, about four or five hundred weight of fine metal is introduced, together with one hundred weight of rich scoriæ or forge cinders (scale-oxide). The metal then fuses, and in this state the workman stirs it about with the poker, so as to expose every part to the flame. The carbon is thus gradually burnt out, partly by the direct action of oxygen in the flame, and partly by cementation with the oxide of iron; and the metal becomes less fusible, and thick and tenacious, so that it sticks together, and is easily formed into four or five large balls, called blooms. In this condition it is removed by tongs, compressed into a cylindrical form by a few blows of a loaded hammer, and quickly converted into a bar, by pressing it between grooved rollers. The tenacity of the metal is further increased by welding several bars together; a faggot of bars is brought to a white heat in an oblong furnace, and then extended between the grooved rollers into a single bar.

The texture of malleable iron is fibrous. Although the purest commercial form of the metal, it still contains about one-half per cent. of carbon, with traces of silicon and other metals.

Pure iron may, however, be obtained by introducing into a Hessian crucible 4 parts of iron wire cut into small pieces, and 1 part of black oxide of iron; placing above these a mixture of white sand, lime, and carbonate of potash, in the proportions used for glass-making; covering the crucible with a closely fitting lid; and exposing it to a very high temperature. A button of pure metal is thus obtained, the traces of carbon and silicon in the iron having been removed by the oxygen of the oxide. (Mitscherlich.)

Steel. — Only the best qualities of malleable iron, those prepared from a pure ore, and reduced by means of charcoal, such as the Swedish iron, are converted into steel. An iron box is filled with flat bars of such iron and charcoal powder, in alternate layers, and kept at a red heat for forty-eight hours, or longer. The surface of the bars is found afterwards to be blistered, and they have absorbed from 1·3 to 1·75 per cent. of carbon. This is the process of cementation. It is known that iron can be converted into steel without being in actual contact with charcoal, provided the iron and charcoal are in a close vessel together, and oxygen be present, the carbon reaching the surface of the metal in the form of carbonic oxide gas. The iron becomes harder by this change, and more fusible, but can still be hammered into shape, and cut with a file. The property in which steel differs most from soft iron, is the capacity it has acquired of becoming excessively hard and elastic, when heated to redness and suddenly cooled by plunging it into cold water or oil. This hardness makes steel invaluable for files, knives, and all kinds of cutting instruments. But the steel, when hardened in the manner described, is harder than is required for most of its applications, and also very brittle. Any portion of its original softness can be restored to the steel by heating it up to particular temperatures, — which are judged of by the colour of the film of oxide upon its surface, which passes from pale yellow at about 430°, through straw yellow, brown yellow, and red purple into a deep blue at 580°, — and allowing the steel afterwards to cool slowly. Articles of steel are *tempered* in this manner.

A simple and expeditious method of converting crude or pig-iron into malleable iron and steel, *without the aid of fuel*, has lately been proposed by Mr. H. Bessemer. This process consists in causing cold air to bubble through the liquid iron; under which circumstances the oxygen of the air combines with the carbon of the iron, removing it in the form of carbonic oxide, and generating sufficient heat to keep the iron in the liquid state without external heating, and to sustain the action till the whole, or any required proportion, of the carbon is burnt away. As the quantity of carbon in the metal diminishes, part of the oxygen combines with the iron, converting it into an oxide, which, at the very high temperature then existing in the vessel, melts, and forms a powerful solvent for the earthy bases associated with the iron. At a certain stage of the process, the whole of the crude iron is said to be converted into cast steel of ordinary quality. By continuing the process, the steel thus formed is gradually deprived of its small remaining portion of carbon, and passes successively from hard to soft steel, steely iron, and ultimately to very soft iron.*

Properties of iron. — Iron is of a bluish-white colour, and admits of a high polish. It is remarkably malleable, particularly at a high temperature, and of great tenacity. Its mean density is 7·7, which is increased by fusion to 7·8439. When kept for a considerable time at a red heat, its particles often form large cubic or

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* Chemical Gazette, 1856, p. 336.

octohedral crystals, and the metal becomes brittle. Malleable iron softens before entering into fusion, and in this state it can be *welded*, or two pieces united by hammering them together. The point of fusion of cast iron is 3479°; that of malleable iron is much higher. Cast-iron expands in becoming solid, and therefore takes the impression of a mould with exactness. Iron is attracted by the magnet at all temperatures under an orange-red heat. It is then itself magnetic by induction, but immediately loses its polarity, if pure, when withdrawn from the magnet. If it contains carbon, as steel and cast iron, it is affected less strongly, but more durably, by the proximity of a magnet, becoming then permanently magnetic. Among the native compounds of iron, the black oxide, which forms the loadstone, and the corresponding sulphide, are those which share this property with the metal in the highest degree. A steel magnet loses it polarity at the boiling point of almond oil; a loadstone, just below visible ignition (Faraday).

Iron reduced from the oxide by hydrogen at a heat under redness, forms a spongy mass, which, when exposed to air, takes fire spontaneously at the usual temperature, oxide of iron being reproduced (Magnus). But iron, in mass, appears to undergo no change in dry air, and to be incapable of decomposing pure water at ordinary temperatures. Nor does it appear to be acted upon by oxygen and water together; but the presence of carbonic acid in the water causes the iron to be rapidly oxidated, with evolution of hydrogen gas. In the ordinary rusting of iron, the carbonate of the protoxide appears to be first produced, but that compound gradually passes into the hydrated sesquioxide, and the carbonic acid is evolved. The rust of iron always contains ammonia, probably absorbed from the air; the native oxides of iron also contain ammonia. Iron remains bright in solutions of the alkalies and in lime-water, which appear to protect it from oxidation; but neutral, and more particularly acid salts, have the opposite effect. The corrosion of iron under water appears, in general, to be immediately occasioned by the formation of a subsalt of that metal with excess of oxide, the acid of which is supplied by the saline matter in solution. Articles of iron may be completely defended from the injury occasioned in this way, by contact with the more positive metal zinc, as in galvanized iron (p. 201), while the protecting metal itself wastes away very slowly. Cast iron is converted into a species of graphite by many years' immersion in sea-water, the greater part of the iron being dissolved while the carbon remains.* In open air, iron burns at a high temperature with vivacity, and its surface becomes covered with a fused oxide, which forms smithy ashes. Iron also decomposes steam at a red heat, and the same oxide is formed as by the combination of the metal in air, namely, the magnetic or black oxide, FeO,Fe_2O_3.

Iron dissolves readily in diluted acids, by substitution for hydrogen, which is evolved as gas. Strong nitric acid acts violently upon iron, yielding oxygen to it, and undergoing decomposition. But the relations of iron to that acid when slightly diluted are exceedingly singular; they have been particularly studied by Professor Schönbein.

Passive condition of iron. — Pure malleable iron, such as a piece of clean stocking wire, usually dissolves in nitric acid of sp. gr. 1·3 to 1·35, with effervescence; but it may be thrown into a condition in which it is said by Schönbein to be *passive*, as it is no longer dissolved by that acid, and may be preserved in it for any length of time without change: — 1. By oxidating the extremity of the wire slightly, by holding it for a few seconds in the flame of a lamp, and after it is cool dipping it gradually in the nitric acid, introducing the oxidated end first. 2. By dipping the extremity of the wire once or twice in concentrated nitric acid, and washing it with water. 3. By placing a platinum wire first in the acid, and then introducing the iron wire, preserving it in contact with the former, which may

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* Mr. Mallett has collected much information respecting the corrosion of iron, in his First Report to the British Association, on the action of sea and river water upon cast and wrought iron, 1839.

afterwards be withdrawn. 4. A fresh iron wire may be introduced in the same manner into the nitric acid, in contact with a wire already passive; this may render passive a third wire, and so on. 5. By making the wire the positive pole or zincoïd of a voltaic battery, introducing it after the negative pole or chloroid has been placed in the acid. Oxygen gas is then evolved from the surface of the iron wire, without combining with it, as if the wire were of platinum. As the passive state can be communicated by contact of passive iron, so it may be destroyed by contact with active iron (or zinc) undergoing, at the moment, solution in the acid. If passive iron be made a negative pole (chlorous) in nitric acid, it also ceases tc resist solution. The indifference to chemical action exhibited by iron when passive, is not confined to nitric acid of the density mentioned, but extends to various saline solutions which are usually acted upon by iron. An indifference to nitric acid of the same kind can also be acquired by other metals as well as iron, particularly by bismuth (Dr. Andrews), but in a much less degree. To account for this remarkable phenomenon various theories have been proposed. Schönbein and Wetzlar attribute it to a peculiar electro-dynamic condition of the surface of the metal, similar to that of the platinum in Grove's gas battery (pp. 208—209). Mousson attributes it to a coating of nitrous acid. By others again it has been ascribed to a peculiar antagonism between two forces acting simultaneously on the metal, the one tending to oxidate it at the expense of the nitric acid, the other to cause it to take the place of hydrogen in the nitrate of water, just as when it dissolves in sulphuric acid.* But perhaps the most probable explanation is that which attributes the passive condition of iron to the formation on its surface of a thin film of anhydrous ferric oxide, similar to specular iron. This view is supported by the fact that iron which has been ignited, and is therefore completely covered with black oxide, exhibits the same characters, excepting that, from the greater thickness of the coating, the passive state is more complete. It may also be observed, that iron becomes passive only in liquids which give up oxygen, and that in the voltaic circuit it becomes passive precisely under the circumstances in which it is exposed to oxidation, *i. e.*, when it is made the zincoid or positive pole, and that it becomes active again when made the negative pole, that is to say, when the oxide is reduced. The same view is supported by the observation that iron rendered passive in nitric acid immediately begins to dissolve on the addition of hydrochloric acid.

PROTOCOMPOUNDS OF IRON; FERROUS COMPOUNDS.

Protoxide of iron, Ferrous oxide; FeO; 36 *or* 450. — Iron appears to admit of three degree of oxidation, the protoxide and sesquioxide, which are both basic and correspond respectively with manganous and manganic oxide, and ferric acid. The protoxide is not easily obtained in a dry state, from the avidity with which it absorbs oxygen. The purest anhydrous protoxide is obtained by igniting the oxalate out of contact of air; but even this, according to Liebig, contains a small quantity of metallic iron. The protoxide exists in the sulphate and other salts of iron, formed when the metal dissolves in an acid with evolution of hydrogen.

Solutions of ferrous salts have a green colour. *Potash* or *soda* added to them throws down the protoxide as a white hydrate, which becomes black on boiling, from loss of water. The colour of the white precipitate changes by exposure to air, to grey, then to green, bluish black, and finally to an ochrey red, when it is entirely sesquioxide. *Ammonia* exercises a similar action, but does not precipitate the whole of the oxide, because the precipitate dissolves in the ammoniacal

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* Dr. Andrews indeed concludes from observation, that the ordinary chemical action of a hydrated acid upon the metals which dissolve in it, is in general diminished, when the acid is concentrated, by the voltaic association of these metals with such metals as gold, platinum, &c.; while, on the contrary, it is increased when the acid is diluted. — Trans. of the Royal Irish Academy, 1838; or, Becquerel, vol. v. pt. 2, p. 187.

salt produced. *Alkaline carbonates* form a precipitate of carbonate of iron, which is white at first, but soon becomes of a dirty green, and undergoes the same subsequent changes from oxidation. Ferrous salts are not precipitated by *hydrosulphuric acid*, the sulphide of iron being dissolved by strong acids, but give a black sulphide with solutions of *alkaline sulphides*. They give a white precipitate with *ferrocyanide of potassium*, which gradually becomes of a deep blue when exposed to air; with the *ferricyanide*, a precipitate which is at once of an intense blue, being one of the varieties of prussian blue. The infusion of *gall-nuts* does not affect a solution of the protoxide of iron when completely free from sesquioxide.

Protosulphide of iron is prepared by heating to redness, in a covered crucible, a mixture of iron filings and crude sulphur, in the proportion of 7 of the former to 4 of the latter. It dissolves in sulphuric and hydrochloric acids, with evolution of hydrosulphuric acid gas (p. 306.).

A *subsulphide of iron*, Fe_2S, appears to be formed when the sulphate of iron is reduced by hydrogen, one-half of the sulphur coming off in the form of sulphurous acid. This subsulphide is analogous to the subsulphides of copper and lead, which crystallize in octahedrons.

Protochloride of iron crystallizes with 4HO, and is very soluble. Like all soluble ferrous salts, it is of a green colour, gives a green solution, and has a great avidity for oxygen.

Protiodide of iron is formed when iodine is digested with water and iron wire, the latter being in excess, and is obtained as a crystalline mass by evaporating to dryness. It was introduced into medical use by Dr. A. T. Thomson. A piece of iron wire is placed in the solution of this salt to preserve it from oxidizing. The protiodide of iron dissolves a large quantity of iodine, without becoming periodide, as the excess of iodine may be precipitated by starch.

Protocyanide of iron, C_2NFe or FeCy, is as difficult to obtain as the protoxide of iron. When cyanide of potassium is added to a protosalt of iron, a yellowish-red precipitate appears, which dissolves in an excess of the alkaline cyanide, and forms the ferrocyanide of potassium (p. 375.). A grey powder remains on distilling the ferrocyanide of ammonium at a gentle heat; and a white insoluble substance on digesting recently precipitated prussian blue in sulphuretted hydrogen water, contained in a well-stopped phial; these products, although they differ considerably in properties, have both been looked upon as protocyanide of iron. This compound is also obtained as a white deposit on boiling an aqueous solution of hydroferrocyanic acid, H_2FeCy_3. The same solution heated with red oxide of mercury forms cyanide of mercury and white protocyanide of iron. The most remarkable property of this cyanide is its tendency to combine with other cyanides of all classes, and to form double cyanides, or to enter as a constituent into the salt-radicals, ferrocyanogen and ferricyanogen, Cy_3Fe and Cy_6Fe_2.

Hydroferrocyanic acid; H_2FeCy_3 or 2HCy,FeCy. This compound was discovered by Mr. Porrett. It may be obtained by decomposing ferrocyanide of barium with sulphuric acid, or ferrocyanide of potassium with an alcoholic solution of tartaric acid, or ferrocyanide of lead with hydrosulphuric acid. It is soluble in water and alcohol, insoluble in ether, and crystallizes by spontaneous evaporation in cubes or four-sided prisms, or sometimes in tetrahedrons. When dry, it may be kept for a long time without alteration in close vessels; but is decomposed on exposure to the air with evolution of hydrocyanic acid, and formation of prussian blue.

Hydroferrocyanic acid unites with most salifiable bases, forming the salts called *ferrocyanides*, whose general formula is M_2FeCy_3, the symbol M denoting a metal. The ferrocyanides of ammonium, potassium, sodium, barium, strontium, calcium, and magnesium, dissolve readily in water; the rest are insoluble or sparingly soluble. Some of them, as the copper and uranium salts, are very highly coloured. Ferrocyanide of potassium has been already described (p. 375.)

Ferrocyanide of potassium and iron; $KFe_2Cy_3 = (KFe),(Cy_3Fe)$.—The bluish-white precipitate which falls on testing a protosalt of iron with the ferrocyanide of potassium or yellow prussiate of potash, *e. g.*, with the protochloride:

$$K_2FeCy_3 + FeCl = KCl + KFe_2Cy_3.$$

It is also obtained in the form of a white crystalline salt (mixed with bisulphate of potash), in the preparation of hydrocyanic acid, by distilling ferrocyanide of potassium with dilute sulphuric acid:

$$2K_2FeCy_3 + 6SO_3 + 6HO = 3(KO,HO,2SO_3) + 3HCy + KFe_2Cy_3.$$

Exposed to the air, it absorbs oxygen and becomes blue. It then affords ferrocyanide of potassium to water, and after all soluble salts are removed, a compound remains, which Liebig names the *basic sesquiferrocyanide of iron*, and represents by the formula $Fe_4.3(Cy_3Fe) + Fe_2O_3$, corresponding, as will be seen hereafter, with 1 eq. of prussian blue + 1 eq. of sesquioxide of iron. This basic compound is dissolved entirely by continued washing, and affords a beautiful deep blue solution. The addition of any salt causes the separation of this compound. Its solution may be evaporated to dryness without decomposition. The white ferrocyanide of iron and potassium likewise turns blue when treated with chlorine-water or nitric acid, being thereby converted into ferricyanide of iron and potassium (KFe_4Cy_6).

$$2KFe_2Cy_3 + Cl = KFe_4Cy_6 + KCl.$$

This latter compound, which when dry is of a beautiful violet colour, may be regarded as ferricyanide of potassium, $K_3Fe_2Cy_6$, in which 2 eq. of potassium are replaced by iron (Williamson).

Ferricyanide of iron, Turnbull's blue; $Fe_3(Cy_6Fe_2)$.—This is the beautiful blue precipitate which falls on adding the ferricyanide of potassium (red prussiate of potash) to a protosalt of iron. It is formed by the substitution of 3 eq. of iron for the 3 eq. of potassium of the latter salt (p. 376). The same blue precipitate may be obtained by adding to a protosalt of iron a mixture of yellow prussiate of potash, chloride of soda, and hydrochloric acid. The tint of this blue is lighter and more delicate than that of prussian blue. It is occasionally used by the calico-printer, who mixes it with permuriate of tin, and prints the mixture, which is in a great measure soluble, upon Turkey-red cloth, *raising* the blue colour afterwards by passing the cloth through a solution of chloride of lime containing an excess of lime. The chief object of that operation is indeed different, namely, to discharge the red and produce white patterns, where tartaric acid is printed upon the cloth; but it has also the effect incidentally of precipitating the blue pigment and peroxide of tin together on the cloth, by neutralizing the acid of the permuriate of tin. This blue is believed to resist the action of alkalies longer than ordinary prussian blue. It is distinguished from prussian blue by yielding, when treated with caustic potash or carbonate of potash, a solution of ferrocyanide of potassium, and a residue of ferroso-ferric oxide:

$$3Fe_5Cy_6 + 4KO = 2K_2FeCy_3 + Fe_3O_4;$$

whereas prussian blue treated in the same manner yields ferric oxide (Williamson).

Carbonate of iron is obtained on adding carbonate of soda to the protosulphate of iron, as a white or greenish-white precipitate, which may be washed and preserved in a humid condition in a close vessel, but cannot be dried without losing carbonic acid and becoming sesquioxide of iron. It is soluble, like the carbonate of lime, in carbonic acid water, and exists under that form in most natural chalybeates. Carbonate of iron occurs also crystallized in the rhombohedral form of calc-spar, forming the mineral *spathic iron*, which generally contains portions of the carbonates of lime, magnesia, and manganese. It is generally of a cream colour or black, and its density rarely exceeds 3·8. This anhydrous carbonate does not absorb oxygen from the air. Carbonate of iron is also the basis of clay iron-stone. There is no carbonate of the sesquioxide.

Protosulphate of iron, Ferrous sulphate, Green vitriol, Copperas; $FeO.SO_3, HO + 6HO$; 76 + 63 *or* 950 + 787·5. — This salt may be formed by dissolving iron in sulphuric acid diluted with 4 or 5 times its bulk of water, filtering the solution while hot, and setting it aside to crystallize. But the large quantities of sulphate of iron consumed in the arts are prepared simultaneously with alum, by the oxidation of iron pyrites (p. 422).

The commercial salt forms large crystals, derived from an oblique rhomboïdal prism, which effloresce slightly in dry air, and, when at all damp, absorb oxygen and become of a rusty red colour; hence the origin of the French term *couperose* applied to this salt, and corrupted in our language into copperas. If these crystals be crushed and deprived of all hygrometric moisture by strong pressure between folds of cotton cloth or filter paper, they may afterwards be preserved in a bottle without any change from oxidation. Of the 7HO which sulphate of iron contains, it loses 6HO at 238°, but retains 1 eq. even at 535°. It may, however, be rendered perfectly anhydrous, with proper caution, without any appreciable loss of acid. The anhydrous salt is also obtained in very small crystalline scales by immersing the hydrated crystals in strong boiling sulphuric acid, and leaving the liquid to cool. The salt was observed by Mitscherlich to crystallize at 176°, with 4HO, in a right rhombic prism, like the corresponding sulphate of manganese. When its solution containing an excess of acid is evaporated by heat, a saline crust is deposited, which, according to Kuhn, contains 3HO. The sulphate of iron appears to form neither acid nor basic salts. One part of copperas requires to dissolve it, the following quantities of water, at the particular temperatures indicated above each quantity, according to the observations of Brandes and Firnhaber:—

50°	59°	75·2°	109·4°	114·°	140·0°	183·2°	194°	212°
1·64	1·43	0.87	0·66	0·44	0·38	0.37	0·27	0·30

Ferrous sulphate undergoes decomposition at a red heat, changing into ferric sulphate, and leaves, after all the acid is expelled, the red sesquioxide known as colcothar. This sulphate, like all the magnesian sulphates, forms with sulphate of potash a double salt containing 6HO. A solution of the sulphate of iron absorbs nitric oxide, and becomes quite black; according to Peligot, it takes up the gas in the proportion of 9 parts to 100 anhydrous salt, or one-fourth of an equivalent (p. 257).

Protonitrate of iron, Ferrous nitrate, may be formed by dissolving the protosulphide in cold dilute nitric acid; the solution evaporated in vacuo yields pale green, very soluble crystals. The solution of the neutral salt is decomposed near the boiling heat, with evolution of nitric acid and copious precipitation of a ferric subnitrate. Iron turnings dissolve in dilute nitric acid and form the same salt, without evolution of gas, the water and acid being decomposed in such a manner as to form ammonia, at the same time that they oxidate the iron.

Protoacetate of iron, Ferrous acetate, is obtained by dissolving the metal or its sulphide in acetic acid. It forms small green prisms which decompose very readily in the air.

Tartrate of potash and iron, Potassio-ferrous tartrate, is prepared by boiling bitartrate of potash with half its weight of iron turnings and a small quantity of water. Hydrogen is evolved, and a white, granular, sparingly soluble salt formed which blackens in the air from absorption of oxygen. It is used medicinally, The iron of this salt is not precipitated by hydrate or carbonate of potash.

SESQUICOMPOUNDS OF IRON; FERRIC COMPOUNDS.

Sesquioxide of iron; Peroxide of iron; Ferric oxide, 80 or 1000. — Occurs very abundantly in nature: 1. as *oligistic* or *specular iron,* in crystals derived from a rhombohedron very near the cube, which are of a brilliant metallic black and highly iridescent. Their powder is red; their density, from 5·01 to 5·22. This oxide forms the celebrated Elba ore. — 2. As *red hematite*, in fibrous, mammillated, or kidney-shaped masses, of a dull red colour, very hard, and of sp. gr. from 4·8 to 5·0. This mineral when cut forms the burnishers of bloodstone.—3. also in combination with water, as *brown hematite*, which is much more abundantly diffused than the anhydrous sesquioxide, the granular variety supplying, according to M. Berthier, more than three-fourths of the iron-furnaces in France. Its density is 3·922; its powder is brown with a shade of yellow, and it dissolves readily in acid, which the anhydrous sesquioxide does not. From analyses by Dr. Thomson and M. Berthier, this mineral appears to unite with 1 eq. of water, as $HO.Fe_2O_3$, analogous to the magnetic oxide of iron, $FeO.Fe_2O_3$. The hydrated sesquioxide produced by the oxidation of iron pyrites, of which it retains the form, contains 1 eq. of water, or 10·31 per cent., and that from the oxidation of the carbonate of iron, 3 eq. of water, or 14·71 per cent., to 2 eq. of sesquioxide (Mitscherlich, *Lehrbuch*, II. 23, 1840). The hydrate is the yellow colouring matter of clay, and with silica and clay it forms the several varieties of ochre.

When metallic iron is oxidated gradually in a large quantity of water, there forms around it a light precipitate of a bright orange yellow colour, which, according to Berzelius, is a ferric hydrate, and of which the empirical formula is $2Fe_2O_3 + 3HO$, the usual composition of brown hematite. When iron is oxidated in deep water, it is converted, according to E. Davy, into the magnetic oxide, which is possibly formed by cementation from the hydrated sesquioxide. The hydrated sesquioxide is also obtained, by precipitation from ferric salts, by ammonia and by hydrated or carbonated alkali; but never pure, as when an insufficient quantity of alkali is added, a sub-salt containing acid is precipitated; and when the alkali is added in excess, a portion of it goes down in combination with the oxide, and cannot be entirely removed by washing. When ammonia is used, the water and excess of the precipitant may be expelled by ignition, and the pure sesquioxide obtained. The latter is not magnetic, and after ignition dissolves with difficulty in acids. When ignited strongly, it loses oxygen and becomes magnetic.

Ferric oxide and its compounds are strictly isomorphous with alumina and the compounds of that earth, and remarkably analogous to them in properties. It is a weak base, of which the salts have a strong acid reaction, and are decomposed by all the magnesian carbonates, as well as by the magnesian oxides themselves. The solution of its salts, which are neutral in composition, have generally a yellow tint; but they are all capable, when rather concentrated, of dissolving a great excess of ferric oxide, and then become red. Very dilute solutions of the neutral salts of ferric oxide are decomposed by ebullition, and the oxide entirely precipitated, the acid of the salt then uniting with water as a base (Scheerer).

Iron is most conveniently distinguished by tests, or precipitated for quantitative estimation, when in the state of sesquioxide. The solution of a ferrous salt is usually oxidized by transmitting a current of chlorine through it, or by adding to it, at the boiling point, nitric acid, in small quantities, so long as effervescence is occasioned from the escape of nitric oxide. *Alkalies* and *alkaline carbonates* throw down a red-brown precipitate of hydrated sesquioxide. *Hydrosulphuric acid* converts a sesquisalt of iron into a protosalt, with precipitation of sulphur. *Ferrocyanide of potassium* throws down prussian blue, but the ferricyanide has no effect upon ferric salts beyond slightly changing the colour of the solution. *Sulphocyanide of potassium* produces a deep wine-red solution with ferric salts, which becomes perfectly colourless when considerably diluted with water, provided the iron salt is not in great excess. *Infusion of gall-nuts* produces a bluish-black precipitate — the basis of common writing ink.

A remarkable insoluble modification of the hydrated sesquioxide is produced by boiling the ordinary hydrate (precipitated from the chloride of ammonia) in water for 7 or 8 hours. The colour then changes from ochre-yellow to brick-red, and the hydrate thus altered is scarcely acted upon by strong boiling nitric acid, and but very slowly by hydrochloric acid. In acetic acid, or dilute nitric or hydrochloric acid, it dissolves, forming a red liquid, which is clear by transmitted, but turbid by reflected light; is precipitated by the smallest quantity of an alkali-salt or a sulphate; and on addition of strong nitric or hydrochloric acid, yields a red granular precipitate which re-dissolves on diluting the liquid with water. The modified hydrate does not form prussian blue with ferrocyanide of potassium and acetic acid. It appears to be $Fe_2O_3.HO$, the ordinary precipitated hydrate, after drying in vacuo, being $2Fe_2O_3.3HO$. This insoluble hydrate is likewise precipitated when a solution of the ordinary hydrate in acetic acid is rapidly boiled. The same solution, if kept for some time at 212° in a close vessel, becomes light in colour, no longer forms prussian blue with ferrocyanide of potassium, or exhibits any deepening of colour on addition of a sulphocyanide; strong hydrochloric or nitric acid, or a trace of an alkali-salt, or sulphuric acid, throws down all the ferric oxide in the form of the insoluble hydrate.* It has also been observed that ferric hydrate becomes crystalline and less soluble by long immersion in water, and by exposure to a low temperature.

Black or magnetic oxide of iron, Ferroso-ferric oxide, $FeO.Fe_2O_3$, an important ore of iron, is a compound of the two oxides. It crystallizes in regular octohedrons. In this compound, the sesquioxide of iron may be replaced by alumina and by oxide of chromium, and the protoxide of iron by oxide of zinc, magnesia, and protoxide of manganese, without change of form. It was produced artificially, by Liebig and Wöhler, by mixing the dry protochloride of iron with an excess of carbonate of soda, calcining the mixture in a crucible, and treating the mass with water. The double oxide then remains as a black powder, which may be washed and dried without further oxidation. The same chemists, by dissolving the black oxide in hydrochloric acid, and precipitating by ammonia, obtained a hydrate of the double oxide. It was attracted by the magnet, even when in the state of a flocculent precipitate suspended in water. When ignited and anhydrous, this double oxide is much more magnetic than iron itself.

Scale-oxide, $6FeO \,.\, Fe_2O_3$.— When iron is heated to redness in contact with air, two layers of scale-oxide are formed, which may be easily separated. The inner layer, which has the composition just given, is blackish grey, porous, brittle, and attracted by the magnet. The outer layer contains a larger proportion of ferric oxide; it is of a reddish iron-black colour, dense, brittle, yields a black powder, and is more strongly attracted by the magnet than the inner layer. The proportion of ferric oxide in the outer layer is between 32 and 37 per cent., and on the very surface as much as 52·8 per cent. (Mosander). The specific gravity of the scale-oxide is 5·48 (Boullay).

Sesquisulphide of iron, or Ferric sulphide, Fe_2S_3, corresponding with the sesquioxide, may be prepared by pouring a solution of a sesquisalt of iron, drop by drop, into a solution of an alkaline sulphide, the latter being preserved in excess. At a low red heat, it loses 2-9ths of its sulphur, and becomes magnetic pyrites. The common yellow iron pyrites is the *bisulphide of iron.* It crystallizes in cubes or other forms of the regular system; its density is 4·981. It may be formed artificially by mixing the protosulphide with half its weight of sulphur, and distilling in a retort at a temperature short of redness. The metallic sulphide combines with a quantity of sulphur equal to that which it already possesses, and forms a bulky powder of a deep yellow colour and metallic lustre, upon which sulphuric and hydrochloric acids have no action. This sulphide appears to be of a stable nature, but the lower sulphides of iron oxidate, when moistened, with great avidity. Stromeyer found the native magnetic sulphide of iron to consist of 100 parts of iron combined with 68 of sulphur; and the sulphide left on distilling iron with sulphur at a high temperature, to be of the same composition. It

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* Péan de St. Giles, *Ann. Ch. Phys.* [3], xlvi. 47.

may be viewed as $5FeS.Fe_2S_3$ (Berzelius). It is said to be this compound which is almost always formed when sulphide of iron is prepared in the usual manner.

Sesquichloride of iron, Ferric chloride, Fe_2Cl_3, is formed when iron is burned in an excess of chlorine. It is volatile at a red heat. Its solution, which is used in medicine, is obtained by dissolving the hydrated sesquioxide of iron in dilute hydrochloric acid. When greatly concentrated, the solution of sesquichloride of iron yields, sometimes orange-yellow crystalline needles, radiating from a centre, which are $Fe_2Cl_3 + 12HO$, at other times, large dark yellowish-red crystals, $Fe_2Cl_3 + 5HO$. Mixed with sal-ammoniac, and evaporated in vacuo, it affords beautiful ruby-red octohedral crystals, consisting of 2 eq. of chloride of ammonium, and 1 eq. of sesquichloride of iron, with 2 eq. of water, $Fe_2Cl_3.2NH_4Cl + 2HO$. Of this water, the double salt loses 1 eq. at 150°, and the other when dried above 300° (Graham). There is a similar double salt, containing chloride of potassium, but not so easily formed. Sesquichloride of iron is soluble both in alcohol and ether. A strong aqueous solution was found by Mr. R. Phillips to dissolve not less than 4 eq. of freshly precipitated ferric hydrate, becoming deep red and opaque.

Sesqui-iodide of iron is formed in similar circumstances to the preceding sesquichloride.

Sesquicyanide of iron, Ferric cyanide, Fe_2Cy_3, is unknown in the pure state. A solution of it, which is decomposed by evaporation, is obtained by precipitating the potash of the red prussiate of fluoride of silicon. It forms a numerous class of double cyanides. A compound of the two cyanides of iron, like the compound oxide, is obtained as a green powder, when a solution of the yellow prussiate of potash, charged with excess of chlorine, is heated or exposed to air. The precipitate should be boiled with eight or ten times its weight of concentrated hydrochloric acid, and well washed. Its formula is, $FeCy.Fe_2Cy_3 + 4HO$.*

Hydroferricyanic acid; $H_3Fe_2Cy_6$, *or* $H_3.(Cy_3Fe)_2$, *or* $3HCy.Fe_2Cy_3$, is obtained by decomposing ferricyanide of lead with sulphuric or hydrosulphuric acid. The decanted yellow solution yields, by careful evaporation, brownish needles, which redden litmus strongly, and have a rough sour taste. This solution gives a deep blue precipitate (Turnbull's blue), with ferrous salts. This acid, united with salifiable bases, forms the *ferricynides*, $M_3Fe_2Cy_6$. The potassium salt is described on p. 376.

Prussian blue, $Fe_3 \cdot 3(Cy_3Fe)$, *or* $3FeCy.2Fe_2Cy_3$. — This remarkable substance is precipitated whenever the yellow prussiate of potash is added to a sesquisalt of iron. Thus with the sesquichloride:

$$3K_2FeCy_3 + 2Fe_2Cl_3 = Fe_4.3(Cy_3Fe) + 6KCl_3.$$

Care must be taken to avoid an excess of the yellow prussiate, as the precipitate is apt to carry down a portion of that salt. The precipitate also contains water which cannot be separated from it without decomposition. On the large scale, prussian blue is sometimes prepared by precipitating green vitriol with yellow prussiate of potash, and subjecting the white precipitate, KFe_2Cy_3, to the action of oxidizing agents, such as chlorine or nitric acid. This process, however, is likely to yield ferricyanide of iron and potassium, KFe_4Cy_6 (p. 40.), rather than prussian blue, properly so called.

Prussian blue, dried at the temperature of the air, is a light porous body, of a rich velvety blue colour; dried at a higher temperature it is more compact, and exhibits in mass a coppery lustre. It is tasteless, and not poisonous. Alkalies decompose it, precipitating sesquioxide of iron and reproducing an alkaline ferrocyanide. This renders prussian blue of little value in dyeing, as it is injured by washing with soap. Red oxide of mercury boiled with prussian blue, affords the soluble cyanide of mercury, with an insoluble mixture of oxide and cyanide of

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* Pelouze, Ann. Ch. Phys. [2], lxix. 40.

iron. Prussian blue is destroyed by fuming nitric acid, but combines with oil of vitriol, forming a white pasty mass, which is decomposed by water.

The combination of prussian blue and sesquioxide of iron, called *basic prussian blue*, was noticed at page 450.

Although there is no *carbonate of the sesquioxide of iron*, the hydrated sesquioxide is dissolved by alkaline bicarbonates, under certain conditions which are not well understood, and a red solution is formed.

Ferric sulphates. — The neutral sulphate, $Fe_2O_3.3SO_3$, is formed by adding to a solution of the protosulphate, half as much sulphuric acid as it already contains, and oxidizing by nitric acid. It gives a syrupy liquid, without crystallizing. This salt is found native in Chili, forming a bed of considerable thickness. It is generally massive, but forms also six-sided prisms, with right summits, which are colourless, and contain 9HO (Rose). Ferric sulphate is soluble in alcohol. It may be rendered anhydrous by a low red heat; but after ignition, it dissolves in water with extreme slowness, like calcined alum.

When hydrated ferric oxide is digested in the neutral sulphate, a red solution is formed, which, according to Maus, is the compound $Fe_2O_3 . 2SO_3$. The rusty precipitate which is formed in a solution of the protosulphate from absorption of oxygen, is another subsulphate, of which the empirical formula is $2Fe_2O_3 . SO_3$. The decomposition may be represented by the following equation: —

$$10(FeO.SO_3) + 5O = 2Fe_2O_3.SO_3 + 3(Fe_2O_3.3SO_3).$$

The neutral ferric sulphate remains in solution.

A *potassio-ferric sulphate*, or *iron alum*, is formed by evaporating a solution of the mixed salts to their point of crystallization. It is colourless and exactly analogous in composition to ordinary alum (p. 422.). Its formula is $KO \cdot SO_3 + Fe_2O_3.3SO_3 + 24HO$.

Another double sulphate is formed, which crystallizes in large six-sided tables, and of which the formula is $2(KO \cdot SO^3) + Fe_2O_3 \cdot 2SO_3 + 6HO$ (Maus), when potash is added gradually to a concentrated solution of ferric sulphate, till the precipitate formed ceases to redissolve, and the solution is evaporated in vacuo.

Berzelius designates as *ferroso-ferric sulphate* a combination containing $FeO \cdot SO_3 + Fe_2O_3 \cdot 3SO_3$. It is the salt produced when a solution of the neutral protosulphate of iron is exposed to the air, till no more ochre is precipitated. The solution, which is yellowish red, does not crystallize, but gives the black oxide of iron when precipitated by an alkali. A salt of the same constituents, but in different proportions, forms large stalactites, composed of little transparent crystals, in the copper mine of Fahlun. This last is represented by $3FeO \cdot 2SO_3 + 3(Fe_2O_3 \cdot 2SO_3) + 36HO$ (Berzelius).

Ferric nitrate. — By dissolving iron in nitric acid, without heat, as in Schœnbein's experiments (page 447), a salt is obtained in large, transparent, colourless crystals. From more than one analysis, Pelouze found the constituents of this salt to be in the proportion of $2Fe_2O_3.3NO_5 + 1\frac{1}{2}HO$. Its solution is decomposed by heat, with deposition of ferric oxide. Ordway*, by digesting metallic iron in nitric acid of sp. gr. 1·20, obtained, first a greenish solution, then a red, and ultimately a rusty brown precipitate; and on adding an equal volume of nitric acid of sp. gr. 1·43 as soon as the last precipitate began to form, and cooling the liquid below 60°, — or by evaporating the greenish solution, adding a large excess of nitric acid and cooling,—colourless, oblique, rhombic prisms, were formed containing $Fe_2O_3 \cdot 3NO_5 + 18HO$; they were deliquescent, sparingly soluble in nitric acid, melted at about 116° to a red liquid, and gave off their acid partly at 212°, completely at a red heat. Two ounces of these crystals pounded and mixed with an equal weight of pulverized bicarbonate of ammonia, produced a fall of tempe-

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* Sill. Am. J. [2], ix. 30.

rature from + 58° to — 5°. By adding this compound to recently precipitated ferric hydrate, Ordway obtained basic salts containing from 1 to 8 eq. oxide to 1 eq. acid. The solutions of these salts were of a deep red colour; were not decomposed by boiling or dilution; but when they contained a large excess of oxide, were decomposed by the addition of chloride of sodium and other salts. Hausmann,* by evaporating the solution of iron in nitric acid to a syrup, adding half the volume of strong nitric acid, and leaving the solution to crystallize, obtained colourless prisms containing $Fe_2O_3.3NO_5 + 12HO$. By mixing a very concentrated solution of this neutral salt with water till the colour became reddish yellow, then boiling, and adding nitric acid after cooling, an ochre-coloured precipitate was formed, containing $8Fe_2O_3 \cdot 2NO_5 + 3HO$. By adding a very large quantity of water to a highly concentrated and slightly acid solution of the nitrate, an ochre-coloured precipitate was sometimes formed, containing $36Fe_2O_3.NO^5 + 48HO$. By treating iron in excess with nitric acid, a precipitate was obtained having the composition $8Fe_2O_3.NO^5 + 12HO$.

Ferric oxalate is very soluble and does not crystallize. It forms a double salt with oxalate of potash, of a rich green colour, of which the formula is $3(KO.C_2O_3) + Fe_2O_3.3C_2O_3 + 6HO$. The crystals effloresce in dry air. In this double salt, the ferric oxide may be replaced by alumina or oxide of chromium. This salt is formed by dissolving hydrated ferric oxide to saturation in bioxalate of potash (salt of sorrel), and crystallizes readily from a concentrated solution. The circumstance of its being the salt of sesquioxide of iron most easily obtained and preserved in a dry state, should recommend it as a pharmaceutical preparation.

The *benzoate and succinate of ferric oxide* are insoluble precipitates. Hence the benzoate and succinate of ammonia are employed to separate iron from manganese. As both these precipitates are dissolved by acids, the iron solution should be made as neutral as possible. The formula of the succinate is, $Fe_2O_3.S$.

Ferric acid, FeO_3. — This compound, which is analogous to manganic acid, is obtained in the form of a potash-salt by exposing metallic iron or ferric oxide to the action of powerful oxidizing agents. 1. A mixture of 1 part iron-filings and 2 parts nitre is projected into a capacious crucible kept at a dull red heat, and the crucible removed from the fire as soon as the mixture begins to deflagrate and form a white cloud; if the heat is too strong, the compound decomposes as fast as it is formed. The soft, somewhat friable mass of ferrate of potash thus obtained, may be taken out with an iron spoon, and preserved in well stoppered bottles; or the ferrate of potash may be obtained in solution by treating the fused mass with ice-cold water, leaving the liquid to stand to allow the undissolved ferric oxide to settle down, and then decanting; the solution must not be filtered, as it is immediately decomposed by contact with organic matter. 2. Ferrate of potash is also formed by igniting ferric oxide with hydrate of potash in an open crucible, or with a mixture of hydrate of potash and nitre. 3. Chlorine gas is passed through a very strong solution of caustic potash containing hydrated ferric oxide in suspension, fragments of solid potash being continually added in order to maintain a large excess of alkali in the liquid. The ferrate of potash, being almost insoluble in the strong alkaline liquid, is deposited in the form of a black powder, which may be freed from the greater part of the mother-liquor by drying it on a plate of porous earthenware. Ferrate of potash is a very unstable compound, and has not been obtained in the crystalline form. Its solution is of a deep red colour, like that of permanganate of potash. The acid has not been obtained in the free state; it appears indeed to be scarcely capable of existing in that state, decomposing, as soon as liberated, into oxygen and ferric oxide. *Ferrate of baryta* is formed by adding a solution of ferrate of potash to a dilute solution of a baryta-salt; it then falls down as a deep carmine-coloured precipitate,

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* Ann. Ch. Pharm. lxxxix. 100.

which may be washed and dried without changing colour. It gives off oxygen when heated, and is readily decomposed by acids.

Nitroprussic acid; $Fe_2Cy_5(NO_2).H_2$. This acid and its salts were discovered by Dr. Lyon Playfair.* It is formed by the action of nitric acid (or rather of nitric oxide) on hydroferrocyanic acid or a ferrocyanide. The hydroferrocyanic acid is first converted into hydroferricyanic acid:

$$4H_2FeCy_3 + NO_2 = 2H_3Fe_2Cy_6 + 2HO + N;$$

and afterwards, by the further action of the nitric oxide, into nitroprussic acid:

$$H_3Fe_2Cy_6 + NO_2 = Fe_2Cy_5(NO_2).H^2 + HCy.$$

Cyanogen is also evolved and oxamide deposited; but these products are due to a secondary action.

To prepare the potassium or sodium salt, ferrocyanide of potassium (2 eq.) is digested in the cold with ordinary nitric acid (5 eq.) diluted with an equal bulk of water, till it is completely dissolved; the solution boiled till it forms with ferrous salts no longer a dark blue, but a green or slate-coloured precipitate, and then left to crystallize, whereupon it deposits a large quantity of nitre, together with oxamide. The strongly coloured mother-liquor is neutralized with carbonate of potash or soda; boiled; filtered to separate a green or brown precipitate; and again left to crystallize. Nitrate of potash or soda then crystallizes out first; and afterwards, by further evaporation, the nitroprussiate. The *sodium-salt* crystallizes most readily, forming large ruby-coloured prisms, which dissolve in 2½ parts of water at 60°, and in a smaller quantity of hot water. From the solution of this salt, the silver-salt may be obtained by double decomposition; and this, when decomposed by hydrochloric acid, yields nitroprussic acid. This acid crystallizes in dark red, very deliquescent, oblique prisms, which dissolve very readily in water, alcohol, and ether. The aqueous solution is very prone to decomposition.

The general formula of the *nitroprussiates* or *nitroprussides* is $Fe_2Cy_5(NO_2).M_2$:† the radical (which might be called *nitroferrocyanogen*) may be regarded as 2 eq. of ferrocyanogen, or 1 eq. of ferricyanogen, Fe_2Cy_6, in which 1 eq. of cyanogen is replaced by nitric oxide, NO_2. Most of them are strongly coloured; the ammonium, potassium, sodium, barium, strontium, calcium, and lead salts, dissolve readily in water, forming deep red solutions from which the salts are not precipitated by alcohol. The other nitroprussiates are insoluble, or sparingly soluble. A solution of a nitroprussiate forms, with the solution of an alkaline sulphide, a splendid blue or purple colour, which affords an extremely delicate test of the presence, either of a nitroprussiate, or of an alkaline sulphide.

QUANTITATIVE ESTIMATION OF IRON.

Iron is always estimated in the form of sesquioxide. If the solution contains protoxide, either alone or mixed with sesquioxide, it is first boiled with a sufficient quantity of nitric acid to convert the whole of the protoxide into sesquioxide, and then treated with ammonia in excess to precipitate the latter. The precipitate is collected on a filter, washed, dried, and ignited at a moderate red heat; too high a temperature expels a portion of the oxygen. Every 10 parts of pure sesquioxide corresponds to 7 parts of metallic iron. In some cases, however, it is necessary to

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* Phil. Trans. 1849, ii. 477.

† This formula was proposed by Gerhardt. Playfair originally gave the formula $Fe_5Cy_{12}(NO)_3.M_5$; and subsequently (*Phil. Mag.* [3.] xxxvi. 360) suggested the simpler formula, $Fe_2Cy_5(NO).M_2$. Gerhardt's formula, however, agrees quite as well with the analyses of the best defined nitroprussiates as either of these, and is more in accordance with certain reactions; viz., that nitroprussiate of sodium, exposed to sunshine, actually gives off nitric oxide; and that when a solution of the barium salt is treated with red oxide of mercury, part of the nitrogen is converted into nitric acid.

use potash as the precipitant. In that case, the precipitated ferric oxide is very apt to carry down with it a portion of the potash, which is exceedingly difficult to remove by washing. It is best therefore, after having washed it two or three times with hot water, to re-dissolve it in acid and precipitate by ammonia. In other cases, as when the solution contains organic matter, the iron must be precipitated by sulphide of ammonium, because such substances prevent the precipitation of the oxide. The precipitated sulphide, after being washed, is then dissolved in nitric acid, and the iron precipitated by ammonia as before.

Volumetric method. — The quantity of iron in a solution may also be estimated by reducing it all to the state of protoxide, either by sulphurous acid or by metallic zinc (in the former case the excess of sulphurous acid must be expelled by boiling), and then adding, from a graduated burette, a quantity of solution of permanganate of potash, sufficient to convert all the protoxide of iron into sesquioxde:

$$KO \cdot Mn_2O_7 + 10FeO = 2MnO + KO + 5Fe_2O_3.$$

The liquid must contain an excess of acid, to hold the oxide of manganese in solution. The first portions of permanganate added produce no visible effect; but as soon as all the protoxide of iron is converted into sesquioxide, the addition of another drop of the permanganate imparts a rose tint to the liquid. The value of the solution of the permanganate must be previously ascertained by dissolving 1 gramme of iron (harpsichord wire) in hydrochloric acid, and determining the number of divisions of the burette occupied by the quantity of the solution required to convert that quantity of iron into sesquioxide. (Margueritte, *Ann. Ch. Phys.* [3], 18, 244.)

The preceding method may also be applied to determine the quantities of protoxide and sesquioxide of iron in a solution when they occur together, — viz., by first treating a portion of the solution, as it is, in the manner just described; then taking another equal portion, reducing all the iron in it to protoxide by sulphurous acid, and applying the same method to the solution thus reduced. The first determination gives the quantity of iron in the state of protoxide; the second, the total quantity present: the difference is therefore the quantity in the form of sesquioxide.

Separation of iron from the metals previously described. — From the *alkalies* and *alkaline earths*, iron is separated by ammonia, after having been brought to the state of sesquioxide. In the case of the alkaline earths, care must be taken to add but a slight excess of ammonia, to filter quickly, and exclude the air as completely as possible during the filtration; otherwise the free ammonia will absorb carbonic acid from the air, and then throw down the earths in the form of carbonates, together with the ferric oxide. Should such precipitation occur, — which may generally be known by the colour of the oxide, — the precipitate must be re-dissolved and the treatment with ammonia repeated. If the solution contains fixed organic substances, such as sugar, tartaric acid, &c., the iron must be precipitated by sulphide of ammonium, and the precipitate treated in the manner already described (p. 457).

From *alumina* and *glucina*, iron is separated by potash, which precipitates the iron, but holds the alumina or glucina in solution. The precipitate, which always contains potash, must then be re-dissolved in acid, and the iron re-precipitated by ammonia.

The separation of iron from *zirconia*, *yttria*, and *thorina*, is effected by adding a sufficient quantity of tartaric acid to prevent the earths from being precipitated when the solution is rendered alkaline, and throwing down the iron by sulphide of ammonium.

From *magnesia* and from *manganous oxide*, iron is most effectually separated by succinate or benzoate of ammonia. The solution, after all the iron has been brought to the state of sesquioxide, is mixed with a sufficient quantity of sal-ammoniac to hold the magnesia or manganous oxide in solution, and very carefully neutralized with ammonia; it is then treated with benzoate or succinate of ammonia, which throws down the iron as ferric benzoate or succinate, leaving the magnesia or manganous oxide in solution. The precipitate is washed and dried, and ignited in an open platinum crucible, so that the air may have sufficient access to it to prevent any reduction of the iron by the carbon of the organic acid. Should such reduction take place, the iron must be re-oxidized by nitric acid. The success of this mode of separation depends entirely on the care with which the acid in the solution is neutralized with ammonia before adding the benzoate or succinate. If too much ammonia has been added, manganese or magnesia goes down with the iron; if too little, a portion of iron remains in solution. The addition of ammonia should be continued till a small quantity of ferric oxide is precipitated, and does not re-dissolve on agitation. The supernatant liquid has then a deep brown colour, the greater part of the iron being still in the solution. The separation of ferric oxide from manganous oxide may also be effected by agitating the solution with excess of carbonate of lime or baryta, which precipitates the iron but not the manganese. According to J. Schiel,* manganese may be separated from iron by mixing the solution with acetate of soda and passing chlorine through it; bioxide of manganese is then alone precipitated. The methods of separation given at page 434, serve very well for preparing a pure salt of manganese from a solution containing that metal together with iron, but are not adapted for quantitative analysis.

Aridium? This name was given by Ullgren to a metal which he believed to exist in the chrome-iron ores of Röros in Sweden, and in the iron ores of Oernstolso. Its characters very much resemble those of iron. It forms two oxides analogous to those of iron, and presenting, both with liquid reagents and with the blowpipe, characters which might be exhibited by oxides of iron containing a little chromium (vid. *Chem. Gaz.* 1854, 289); Bahr (*Ann. Ch. Pharm.* lxxxvii. 264), endeavoured to prepare the supposed new metal by Ullgren's process, and came to the conclusion that it was merely iron containing a little phosphorus, and perhaps also chromium.

SECTION III.

COBALT.

Ep. 29·52, *or* 369; Co.

Cobalt occurs in the mineral kingdom chiefly in combination with arsenic, as arsenical cobalt, CoAs; or with sulphur and arsenic, as grey cobalt ore, $CoAs.CoS_2$, but contaminated with iron, nickel, and other metals. Its name is that of the Kobolds or evil spirits of mines, and was applied to it by the superstitious miners of the middle ages, who were often deceived by the favourable appearance of its ores. These remained without value, till the middle of the sixteenth century, when they were first applied to colour glass blue. They are now consumed in great quantity for the blue colours of porcelain and stoneware. Cobalt is likewise found in almost all meteoric stones.

To obtain metallic cobalt, the native arsenide is repeatedly roasted, by which the greater part of the arsenic is converted into arsenious acid, and carried off in vapour, while the impure oxide of cobalt, known as *zaffre*, remains. This is dissolved in hydrochloric acid, and the remaining arsenic precipitated as sulphide, by passing a stream of sulphuretted hydrogen through the solution. To get rid

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* Sell. Am. J. [2], xv. 275.

of the iron present, the last solution, after filtration, is boiled with a little nitric acid, to peroxidize that metal; and carbonate of potash is added in excess, which throws down carbonate of cobalt and sesquioxide of iron. The precipitate is treated with oxalic acid, which forms an insoluble oxalate of cobalt and soluble ferric oxalate. The oxalate of cobalt is dried and decomposed by ignition in a covered crucible, when the oxide is reduced by the carbon of the acid, which goes off as carbonic acid, while the metallic cobalt remains as a black powder. To separate cobalt from nickel, with which it is almost always associated, the mixed oxalates of cobalt and nickel, obtained by the preceding process, are dissolved in ammonia, after which the liquid is diluted and exposed to the air in a shallow basin for several days. The ammonia evaporates, and the salt of nickel precipitates as a green powder, while the salt of cobalt remains in solution. The liquid is then decanted, and if no additional precipitate subsides from it in twenty-four hours, it is free from nickel, and may be evaporated to dryness. The precipitate of nickel contains a little cobalt.*

Cobalt is a brittle metal, of a reddish grey colour, somewhat more fusible than iron, and of the density 8·5131 (Berzelius). Rammelsberg, in five experiments with cobalt reduced by hydrogen, found the specific gravity to vary from 8·132 to 9·495; the mean is 8·957. Pure cobalt is magnetic, but a minute quantity of arsenic causes it to lose that property.

Cobalt is less oxidable in the air or by acids than iron, dissolving slowly in diluted hydrochloric or sulphuric acid, when heated, with evolution of hydrogen; but it is readily oxidized by nitric acid. This metal forms a protoxide and sesquioxide, CoO, and Co_2O_3, corresponding with the oxides of iron, and three intermediate oxides, viz., $Co_3O_4 = CoO.Co_2O_3$; $Co_6O_7 = 4CoO.Co_2O_3$; and $Co_8O_9 = 6CoO.Co_2O_3$. According to Fremy, the first of these, viz., Co_3O_4 is a salifiable base combining directly with acetic acid, and existing in several ammonio-salts of cobalt. Fremy has also obtained compound salts of this nature containing a bioxide of cobalt CoO_2.

Protoxide of cobalt, Cobaltous oxide, CoO, 37·52 *or* 469. — Prepared by the ignition of the carbonate. This oxide is a powder of an ash-grey colour. It colours glass blue, even when in minute quantity, no other colouring matter having so much intensity. *Smalt blue* is a pounded potash-glass containing cobalt. All compounds of cobalt, when heated with *borax* or *phosphorous-salt*, either in the inner or in the outer blow-pipe flame, impart a splendid blue colour to the bead. This coloration affords an extremely delicate test for cobalt.

The salts of protoxide of cobalt have a reddish colour in solution. *Potash* or *soda* added to these solutions forms a blue precipitate of the hydrated oxide, insoluble in excess of the reagent. *Ammonia* also forms a blue precipitate, which dissolves in excess of ammonia, yielding a red-brown solution. If the cobalt solution contains a large quantity of free acid or of an ammonical salt, no precipitate is formed by ammonia. *Alkaline carbonates* precipitate a pink carbonate of cobalt, soluble in *carbonate of ammonia*. *Hydrosulphuric acid* does not precipitate a solution of cobalt containing either of the stronger acids; but in a solution of acetate of cobalt, or of any cobalt-salt mixed with acetate of ammonia, it forms a black precipitate of protosulphide of cobalt. *Alkaline sulphides* throw down the same precipitate from all solutions of protoxide of cobalt.

Oxide of cobalt appears to combine with alkalies and earths as well as with acids. It dissolves in fused potash, and imparts a blue colour to the compound. Magnesia mixed with a drop of nitrate of cobalt, and then dried and ignited, assumes a feeble but characteristic rose tint. A compound of oxide of cobalt with alumina is obtained by mixing the solution of a salt of cobalt, which must be perfectly free from iron or nickel, with a solution of equally pure alum, precipitating the liquor by an alkaline carbonate, washing the precipitate with care,

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* For other methods of separating nickel and cobalt, see *Nickel*.

then drying and igniting it strongly. It forms a beautiful blue pigment, known as cobalt-blue, which may be compared in purity of tint with ultramarine. A compound of oxide of cobalt with oxide of zinc of a fine green colour may be prepared in a similar manner. These coloured compounds often afford useful confirmatory tests of the presence of zinc, alumina, or magnesia. The substance to be examined is placed on platinum foil, moistened with nitrate of cobalt, then dried, and strongly heated in the blow-pipe flame.

Chloride of cobalt, $CoCl$, is obtained by dissolving zaffre or the oxide in hydrochloric acid. Its solution is pink-red, and affords hydrated crystals of the same colour; but when highly concentrated, assumes an intense blue colour, and then affords blue crystals of chloride of cobalt, which are anhydrous (Proust). The red solution is used as a sympathetic ink; characters written with it on paper are colourless and invisible, or nearly so, but when the paper is warmed by holding it near a fire or against a stove, the writing becomes visible and appears of a beautiful blue. After a while, as the salt absorbs moisture, the colour again disappears, but may be reproduced by the action of heat. If the paper be exposed to too high a temperature, the writing becomes black, and does not afterwards disappear. The addition of a salt of nickel to the sympathetic ink gives a green instead of blue.

The neutral *carbonate of cobalt* is unknown, oxide of cobalt, like magnesia, being thrown down from its solutions by alkaline carbonates, as a carbonate with excess of oxide. The sub-carbonate of cobalt is a pale red powder, which contains, according to Setterberger, 2 eq. of carbonic acid, 5 eq. of oxide of cobalt, and 4 eq. of water.

Besides the *sulphate of cobalt* corresponding with green vitriol, another salt was crystallized by Mitscherlich between 68° and 86°, containing 6 eq. of water, $CoO.SO_3+6HO$, isomorphous with a corresponding sulphate of magnesia. Sulphate of cobalt forms the usual double salts with the sulphates of potash and ammonia, containing $6HO$.

Nitrate of cobalt, $CoO.NO_5$ — is obtained by dissolving the metal, the protoxide, or the carbonate in dilute nitric acid. Its solution is carmine-coloured, and on evaporation yields red crystals containing 6 eq. of water; they deliquesce in the air, fuse below 100°, and at a higher temperature give off water and melt into a violet-red liquid, which afterwards becomes green and thick, and is ultimately converted, with violent intumescence and evolution of nitrous fumes, into black sesquioxide of cobalt. Characters written on paper with a solution of this salt assume a peach-blossom colour when heated.

A *sexbasic nitrate*, $6CoO.NO_5+5Aq$, is obtained on adding excess of ammonia to a well boiled solution of the neutral nitrate, carefully protected from the air. It then falls down as a blue precipitate, but on the slightest access of air quickly assumes a grass-green colour and partly redissolves in the liquid.

Cobalt-yellow, $CoO.KO.N_2O_8$.—This compound is formed by adding a solution of nitrite of potash (obtained by passing the nitrous fumes evolved from a heated mixture of nitric acid and starch into caustic potash) to an acid solution of nitrate of cobalt; nitric oxide and nitrate of potash are then formed, and the cobalt-compound separates in the form of a beautiful yellow crystalline powder:

$$CoO.NO_5 + 2NO_5 + 4(KO.NO_3) = 3(KO.NO_5) + 2NO_2 + N_2O_8.CoO.KO.$$

It is likewise obtained by adding potash, not in excess, to solution of nitrate of cobalt, so as to precipitate a blue basic salt, treating this with a slight excess of nitrite of potash, and adding nitric acid in a thin stream, by means of a pipette. Also by treating nitrate of cobalt with a slight excess of potash, so as to throw down the rose-coloured hydrated oxide, and passing nitric oxide gas into the mixture. This last reaction is so rapid that it may be exhibited as a lecture-experiment. The compound crystallizes in microscopic four-sided prisms with pyramidal summits. It is insoluble in cold water, also in alcohol and ether, but when boiled with water gradually dissolves with evolution of acid vapours; the solution yields on evaporation a lemon-yellow salt of different composition. Nitric acid and hydrochloric acid do not act upon it in the cold, but decompose it at a boiling heat, with evolution of nitrous fumes. Hydrosulphuric acid decomposes it very slowly, sulphide of ammonium immediately, forming black sulphide of cobalt. When heated, it assumes an orange-yellow colour, gives off water and afterwards fumes of nitric and hyponitric acids, and leaves sesquioxide of cobalt mixed with nitrite of potash. Its beautiful colour, its permanence, and the facility with which it mixes with other colours, render it well adapted for artistic purposes.*

According to A. Stromeyer,† this salt is a nitrite of cobaltic oxide and potash, $Co_2O_3.2NO_3 + 3(KO.NO_3)$, and its formation may be represented by the equation,

$$2(CoO.SO_3) + 5(KO.NO_3) + O = [Co_2O_3.2NO_3 + 3(KO.NO_3)] + 2(KO.SO_3).$$

When a solution of lead is mixed with nitrite of potash and acetic acid, the liquid assumes a yellow colour, but no precipitation takes place; but on adding a cobalt-salt, a yellowish green precipitate (or brownish black and crystalline from dilute solutions) is formed, whose composition is that of the yellow cobalt-compound with half the potash replaced by oxide of lead (Stromeyer).

Phosphate of cobalt, $2CoO.HO.PO_5$, is an insoluble precipitate of a deep violet colour. When 2 parts of this phosphate or 1 part of the arseniate of cobalt are carefully mixed with 16 parts of alumina and strongly ignited for a considerable time, a beautiful blue pigment is obtained, resembling ultramarine; it was discovered by Thénard.

Arseniate of cobalt, $3CoO.AsO_5 + 8HO$, exists as a crystalline mineral called *cobalt-bloom*.

Sesquioxide of cobalt, Cobaltic oxide, Co_2O_3, is formed when chlorine is transmitted through water in which the hydrated protoxide is suspended, or when a salt of the protoxide is precipitated by a solution of chloride of lime. In the former case, water is decomposed by the chlorine, and hydrochloric acid produced, while the oxygen of the water peroxidizes the cobalt;

$$2CoO + HO + Cl = Co_2O_3 + HCl.$$

The sesquioxide of cobalt is precipitated as a black hydrate, containing 2HO. This hydrate, when cautiously heated to 600° or 700°, yields the black anhydrous oxide. When sesquioxide of cobalt is digested in hydrochloric acid, chlorine is evolved, and the protochloride formed. Exposed to a low red heat, the sesquioxide loses oxygen, and the compound oxide, $CoO.Co_2O_3$, is produced. (Hess.) When protoxide of cobalt is calcined with a borax glass, at a moderate heat, it absorbs oxygen, and a black mass is obtained, which, mixed with manganic oxide, serves as a black colour in enamel painting.

Sesquioxide of cobalt acts as a weak base. Phosphoric, sulphuric, nitric, and hydrochloric acids dissolve its hydrate in the cold, without decomposition at first, but the resulting salts are afterwards reduced to salts of the protoxide. A proto-salt of cobalt containing a small quantity of a sesquisalt is somewhat deepened in colour. The most permanent of the sesquisalts is the acetate; the hydrated sesquioxide while yet moist dissolves in acetic acid, slowly but completely. The solution, which has an intense brown colour, forms a brown precipitate with alkalies and alkaline carbonates. With ferrocyanide of potassium it forms a dark precipitate, which, if the precipitant is in excess, gives up cyanogen to it, converting it into ferricyanide of potassium and being itself converted into green ferrocyanide of cobalt. Alkaline oxalates colour the solution yellow, forming an oxalate of the oxide Co_3O_4.

According to Fremy, the oxide Co_3O_4 combines also with other acids. The

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* St. Evre, Ann. Ch. Phys. [3], xxxviii. 177.

† Ann. Ch. Pharm. xcvi. 218.

acetate of this oxide is obtained by digesting in dilute acetic acid the hydrated oxide obtained by continued action of oxygen on the blue precipitate thrown down from ordinary cobalt-salts by potash not in excess. Fremy also states that when chlorine is passed into the solution of ordinary acetate of cobalt, a brownish yellow salt is formed containing the base Co_3ClO_3, or Co_3O_4 in which 1 eq. of O is replaced by Cl. This chlorine base exists also in some of the ammonio compounds of cobalt (pp. 463–66). The oxide Co_3O_4 is obtained in the free state by heating the nitrate or oxalate of cobalt, or the hydrated sesquioxide to redness in contact with the air (Hess, Rammelsberg); but according to Beetz and Winkelblech, the oxide thus obtained is Co_6O_7. When the residue obtained by gently igniting the oxalate in contact with the air is digested in strong boiling hydrochloric acid, the oxide Co_3O_4 remains in hard, brittle, greyish-black microscopic octohedrons, having a metallic lustre. The same crystalline compound is obtained by igniting dry protochloride of cobalt, alone or mixed with sal-ammoniac, in dry air or oxygen gas (Schwarzenberg).

A *cobaltic acid*, Co_3O_5, is obtained in combination with potash by strongly igniting the oxide Co_3O_4, or the protoxide, or the carbonate, with pure hydrate of potash. A crystalline salt is then formed which, when dried at 100° C., contains $KO.3Co_3O_5+3HO$, and gives of 1 eq. of water at 130° (Schwarzenberg).

Bioxide of cobalt, CoO_2, has not been obtained in the free state, but exists, according to Fremy, in the oxycobaltiac salts.

There exist three *sulphides of cobalt*, a protosulphide, sesquisulphide, and bisulphide.

Sesquicyanide of cobalt has not been obtained in the separate state, but it exists in a class of double cyanides, of which the radical is cobalticyanogen, Cy_6Co_2, analogous to ferricyanogen. The cobalticyanide of potassium, corresponding with the red prussiate of potash, is formed when protoxide of cobalt or its carbonate is dissolved in caustic potash which has been treated with an excess of hydrocyanic acid. It is an anhydrous salt, pale yellow and nearly colourless when pure, and of the same form as the ferricyanide of potassium. Its solution does not affect the salts of iron, but forms a rose-coloured precipitate with those of the protoxide of cobalt.*

A *phosphide of cobalt*, Co_3P, was obtained by Rose, as a grey powder, on passing hydrogen over the subphosphate of cobalt ignited in a porcelain tube. It is also produced by the action of phosphuretted hydrogen on the chloride of cobalt, and may be looked upon as analogous in composition to the former compound, H_3P.

Ammoniacal salts of cobalt.—Cobalt-salts treated with excess of ammonia in a vessel from which the air is excluded, unite with the ammonia, forming compounds to which Fremy gives the name of *ammonio-cobalt salts*. Most of them contain 3 eq. ammonia to 1 eq. of the cobalt-salt; thus the chloride contains $CoCl.3NH_3+HO$: the nitrate $CoO.No_5.3NH_3+2HO$. They are mostly crystallizable and of a rose-colour, soluble without decomposition in ammonia, but decomposed by water with separation of a basic salt. (Fremy.) H. Rose, by treating dry chloride of cobalt with ammoniacal gas, obtained the compound $CoCl.2NH_3$; and similarly an anhydrous sulphate containing $CoO.SO_3.3NH_3$.

When an ammoniacal solution of a cobalt salt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed containing a higher oxide of cobalt (Co_2O_3 or CO_2), and therefore designated generally as *peroxidized ammonio-cobalt salts*. Several of these salts containing different bases are often formed at the same time. Fremy† distinguishes four classes of these compounds, viz., salts of *oxycobaltia*, *luteocobaltia*, *fuscocobaltia*, and *roseocobaltia*.

The *oxycobaltia-salts* are formed by the action of the air on concentrated solu-

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* For further details on the cobalticyanides, *vide* Gmelin's Handbook (translation), vii. 492–497.

† Ann. Ch. Phys., [3], xxxv. 257; Chem. Gaz. 1853, 201.

tions of ammonio-cobalt salts. They have generally an olive colour, are sparingly soluble in the ammoniacal liquid, and are decomposed by water, especially when hot, with evolution of pure oxygen, liberation of ammonia, and separation of a green basic salt containing cobaltoso-cobaltic oxide, CO_3O_4. They contain 5 eq. of ammonia associated with 2 eq. of a monobasic salt of bi-oxide of cobalt, CoO_2; thus the nitrate is composed of $2(CoO_2.NO_5).5NH_3$. The nitrate and sulphate crystallize in small prisms containing water of crystallization (Fremy).

The *luteocobaltia-salts* are formed: 1. By the action of the air on dilute solutions of ammonio-cobalt salts; 2. By the action of a small quantity of water on crystallized oxycobaltia-salts; 3. By treating the brown solution, formed by the action of oxygen in excess on ammonio-cobalt salts, with dilute acids; 4. By treating roseocobaltia-salts with excess of ammonia. These salts are of a fine yellow colour, crystallize readily, are tolerably permanent, and resist for some time the action of boiling water. They give no precipitates with alkaline phosphates or carbonates at ordinary temperatures, but are decomposed by boiling potash, with evolution of ammonia and separation of Co_2O_3HO. Dilute acids precipitate them from their aqueous solution in the crystalline state. They contain 1 eq. of a sesquisalt of cobalt, associated with 6 eq. of ammonia; thus, the sulphate $= (Co_2O_3.3SO_3).6NH_3$; the chloride $= Co_2Cl_3.6NH_3$. (Fremy.) This last salt was previously obtained by Rogojski,* who regarded it as the *hydrochlorate of dicobaltinamine* $ClH.N_2H_5co$ [$co = \frac{2}{3}Co$]. He likewise obtained the other salts of the same base by double decomposition.

Fuscocobaltia-salts are formed when an ammoniacal solution of a protosalt of cobalt is exposed to the air, and by the action of water on the oxycobaltia-salts. They are all uncrystallizable, but may be obtained in the solid state by precipitation with alcohol or excess of ammonia. They are slowly decomposed by boiling with water, but quickly on the addition of an alkali, with evolution of ammonia, and precipitation of hydrated sesquioxide of cobalt. They are of a brown colour, and appear to contain basic salts of sesquioxide of cobalt, united with 4 or 5 eq. of ammonia. The nitrate contains $Co_2O_3.2NO_5.4NH_3.3HO$.

Ammonio-chloride of cobalt, after exposure to the air, yields by evaporation in vacuo, an uncrystallizable residue having the characters of the fuscocobaltia-salts, but containing a chlorine-base; its formula is $Co_2Cl_2O.4NH_3.3HO$. By exposing the solution of the ammonio-chloride to the air for two or three weeks, and then boiling with sal-ammoniac, roseocobaltiacal chloride separates out first, and afterwards a black crystalline compound containing $Co_3ClO_3.NH_3 + 5HO$.

The *roseocobaltia-salts* are obtained: 1. By slightly acidulating the solution of an ammonio-cobalt salt, which has been exposed to the air; 2. By boiling the solution of an ammonio-cobalt salt, which has been exposed to the air for two or three days, and contains a fuscocobaltia salt, with a salt of ammonia; 3. By mixing oxycobaltia-salts with boiling solutions of ammoniacal salts. They have a fine red or rose colour, and some of them crystallize readily. Their reactions are similar to those of the luteocobaltia-salts. The nitrate and the neutral sulphate contain 3 eq. of $Co_2O_3.3NO_5$, or $Co_2O_3.3SO_3$, with 5 eq. ammonia. There is also an acid sulphate containing $(Co_2O_3.5SO_4)\ 5NH_3 + 5HO$, obtained by adding sulphuric acid in excess to an ammoniacal solution of sulphate of cobalt which has stood for some days in contact with the air. Baryta-water added to the solution of the sulphate, throws down roseocobaltiacal oxide, which is rose-coloured, has a strong alkaline reaction, and decomposes on boiling, giving off ammonia and depositing Co_2O_3. The chloride, $Co_2Cl_3.5NH_3.HO$, is obtained by boiling the ammonio-chloride of cobalt, or the chlorine-compound $Co_2Cl_2O\ 4NH_3$ (p.464), or a salt of oxycobaltia, with chloride of ammonium (Fremy).

Genth † and F. Claudet ‡ have also described a compound which appears to be

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* J. pr. Chem. lvi. 491.

† Ann. Ch. Pharm. lxxx. 275; Chem. Gaz. 1851, 266.

‡ Phil. Mag. [4], ii. 253; Chem. Soc. Qu. J. iv. 355.

the same as Fremy's hydrochlorate of roseocobaltia, although each assigns to it a different formula. When sulphate or chloride of cobalt is mixed with a large quantity of chloride of ammonium and an excess of ammonia, exposed for some time to the air, and then boiled with excess of hydrochloric acid, a crimson powder gradually separates, oxygen is evolved, and the liquid becomes colourless. This compound dissolves in 244 parts of cold water, and in a smaller quantity of boiling water, but is decomposed by continued boiling, unless hydrochloric acid be added; in that case a solution is obtained, from which the compound crystallizes on cooling in ruby-coloured regular octohedrons. Genth assigns to this compound the formula $Co_2O_3.3NH_4Cl$, regarding it as the chloride of a conjugated radical $Co_2O_3.3NH_4$. Claudet finds it to contain 3Cl,2Co, 5N and 16H, and expresses its composition by one of the following formulæ: —

$$3NH_4Cl+2NH_2Co; \qquad Cl\left\{\begin{matrix}NH_2Co_2\\NH_3NH_4\\NHNH_4\end{matrix}\right\}; \qquad ClN\left\{\begin{matrix}H_2\\Co_2\end{matrix}\right\}+2ClN\left\{\begin{matrix}H_2\\NH_4\end{matrix}\right\}.$$

According to the two latter formulæ, the compound is supposed to contain ammonium in which part of the hydrogen is replaced by NH_4. It might also be regarded as the *hydrochlorate of pentacobaltosamine* $N_5H_{13}Co_2.3HCl$, the base being formed of 5 eq. of ammonia in which 2 eq. of hydrogen are replaced by cobalt. Gregory* assigns to it the formula $Co_2Cl_3.5NH_3$, making it identical with Fremy's roseocobaltiacal chloride.

The compound heated in a glass tube gives off ammonia and sal-ammoniac, and leaves CoCl. When the aqueous solution is boiled, ammonia is evolved, and a precipitate formed probably consisting of $Co_3O_4.3HO$, combined with nitride of cobalt. The chlorine compound treated with recently precipitated oxide of silver, yields the oxygen-compound of the same radical; and by double decomposition with various silver-salts, the other salts of the base.

The ammonia in all these compounds is in a peculiar state, not exhibiting its usual basic properties, or being recognisable by the usual reagents or replaceable by other bases. Claus attributes this circumstance to the ammonia being in a *passive* state, which is merely another way of expressing the fact, but affords no explanation. Weltzien supposes the compounds in question to contain compound ammonium-molecules, in which 1 or 2 at. hydrogen are replaced by ammonium itself (an idea first suggested by Mr. Graham), viz., *ammo-cobaltammonium* $\overbrace{NH_2AmCo}$, and *biammo-cobaltammonium* $\overbrace{NHAm_2Co}$ [the symbol Am standing for NH_4]. Thus the *ammoniocobalt salts*, containing $2NH_3$, may be regarded as neutral salts of ammo-cobaltammonium, and those which contain $3NH_3$ as neutral salts of biammo-cobaltammonium: thus —

$$CoCl.2NH_3 = \overbrace{NH_2AmCo}.Cl; \text{ and}$$

$$CoBr.3NH_3 = \overbrace{NHAm_2Co}.Br.$$

The *fuscocobaltia-salts* may be regarded as basic salts of the sesquioxide of ammo-cobaltammonium, *e. g.* —

$$Co_2O_3.2NO_5.4NH_3 = (\overbrace{NH_2AmCo})_2O_3.2NO_5.$$

The *luteocobaltia*-salts, as neutral salts of the sesquioxide of biammo-cobaltammonium, *e. g.* —

$$Co_2O_3.3NO_5.6NH_3 = (\overbrace{NHAm_2Co})_2O_3.3NO_5;$$

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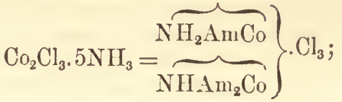
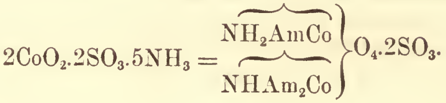
* Ann. Ch. Pharm. lxxxvii. 125.

The *roseocobaltia*-salts as neutral sesquisalts containing 1 at. of each of the above-mentioned ammoniums, thus —



$$Co_2Cl_3.5NH_3 = \left.\begin{array}{c}\overbrace{NH_2AmCo}\\ \overbrace{NHAm_2Co}\end{array}\right\}.Cl_3;$$

And the *oxycobaltia-salts* as basic salts of the same two ammonium-molecules, *e.g.* —



$$2CoO_2.2SO_3.5NH_3 = \left.\begin{array}{c}\overbrace{NH_2AmCo}\\ \overbrace{NHAm_2Co}\end{array}\right\}O_4.2SO_3.$$

ESTIMATION OF COBALT, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Cobalt is generally precipitated from its solutions by caustic potash. The precipitate is bluish, and consists of a basic salt, which, however, when heated, is converted into the hydrated protoxide of a dingy rose colour. It must then be washed in hot water, dried and ignited in an atmosphere of hydrogen, by which it is reduced to the metallic state, after which it is weighed. According to Beetz,* the reduction to the metallic state may be dispensed with, an accurate result being obtained by igniting the precipitated oxide till it no longer varies in weight, its composition being then $4Co.Co_2O_3$ or Co_6O_7; but the reduction by hydrogen is perhaps the surer method.

Cobalt is separated from the *alkalies* and *alkaline earths* by sulphide of ammonium, the black sulphide of cobalt being then dissolved in nitro-hydrochloric acid, and the oxide precipitated by potash as above.

From *magnesia* it may also be separated by sulphide of ammonium, sufficient chloride of ammonium being added to hold the magnesia in solution.

From *alumina* and *glucina* it is separated by potash.

The separation of cobalt from *manganese* is difficult. It is best effected by heating the mixed oxides in hydrochloric acid gas, which converts them into chlorides, and then heating the chlorides in a stream of hydrogen, which reduces the cobalt to the metallic state, but leaves the chloride of manganese undecomposed; the latter is then dissolved out by water. Another mode of separation is to digest the mixed oxides in a solution of pentasulphide of calcium, which dissolves the sulphide of cobalt, but leaves the sulphide of manganese undissolved.†

Cobalt is separated from *iron* in the same manner as manganese (p. 458), viz., by bringing the iron to the state of sesquioxide, then adding chloride of ammonium, neutralizing with ammonia, and precipitating the iron by succinate of ammonia.

SECTION IV.

NICKEL.

Eq. 29·57 *or* 369·6.

This metal resembles iron and cobalt more than any others, and is associated with these metals in meteorites, and in most of the terrestrial minerals which contain it. The principal ore of nickel is arsenical nickel, a mineral having the colour of metallic copper, to which the German miners, having attempted in vain

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* Pogg. Ann. lxi. 472.

† Cloez, J Pharm. [3,] vii. 157.

to extract copper from it, gave the name *kupfer-nickel*, or false copper. This mineral was found by Cronstedt of Sweden, in 1751, to contain a particular metal, which he called nickel. Nickel imparts a remarkable whiteness to the metallic alloys which contain it, on which account it has come of late to be valued in the arts, being added to brass to form the well-known imitations of silver.

The metal is prepared from the native arsenide, or from an artificial arsenide called *speiss*, which contains about 54 per cent. of nickel, and has been observed by Wöhler to occur in octohedrons with a square base, having the composition Ni_3As. Speiss is a metallic substance which collects at the bottom of the crucibles in which smalt or cobalt-blue is prepared. In that operation, a mixture of quartzy sand, potashes, and the roasted ore of cobalt is fused. The previous roasting never being perfect, a part of the metals escapes oxidation; and hence when the mixture described is fused, the cobalt, which is more oxidable than nickel and copper, reacts upon the oxides of these metals, and reduces them, while it is itself oxidated: the nickel and copper concentrate in the speiss, while the smalt contains scarcely any of them. A salt of nickel may be obtained by treating speiss in fine powder with an equal weight of sulphuric acid, diluted with four or five times its bulk of water, and gradually adding an equal weight of nitric acid, which occasions the oxidation of both the nickel and the arsenic. The green solution thus obtained, when cooled and allowed to stand for twenty-four hours, deposits much arsenious acid, from which it may be separated by filtration. A quantity of carbonate of potash, equal to half the weight of the speiss, is then added to the solution, which is concentrated and set aside to crystallize. The double sulphate of nickel and potash, $NiO.SO_3 + KO.SO_3 + 6HO$, forms easily, and may be obtained free from arsenic by a second crystallization. (Dr. Thomson.) The perfect separation of small quantities of cobalt and copper, which these crystals may still contain, requires additional processes.* With the view of obtaining the metal, the insoluble oxalate of nickel may be precipitated from the preceding salt by oxalate of ammonia, washed, dried, and ignited gently in a covered crucible. The oxalic acid reduces the oxide of nickel, and the metal remains in a spongy state. It is pyrophoric, like manganese and iron prepared in the same manner, if the temperature of reduction has been low. To obtain the metal in a solid mass, it should be fused in a crucible covered with pounded glass. The oxide of nickel is very easily reduced both by carbonic oxide and by hydrogen.

Nickel, when free from cobalt, is silver-white, unalterable in air, and highly ductile. Its density, according to Richter, is 8·279, and after being forged 8·666. Nickel is magnetic nearly to the same extent as iron. Magnets composed of this metal lose their polarity at 630° (Faraday). It is somewhat more fusible than iron. Nickel forms two oxides corresponding with the protoxide and sesquioxide of iron; but the double compound of the two oxides of nickel, corresponding with the black oxide of iron, has not been observed.

Protoxide of nickel, NiO, 37·57, or 469·6, may be obtained by the ignition of the carbonate or nitrate of nickel, or by precipitation from its salts by an alkali, as a dark ash-coloured powder, or as a bulky hydrate of an apple-green colour, NiOHO. Oxide of nickel is very soluble in acids, but not in potash or soda. Ammonia dissolves it, and forms an azure-blue solution, from which oxide of nickel is precipitated by potash, baryta, and strontia, having a considerable tendency to combine with salifiable bases. The solutions of its salts have all a green colour, much more intense than that of the ferrous salts. They are not precipitated by hydrosulphuric acid when a strong acid is present, but afford a black sulphide with alkaline sulphides. Carbonate of nickel is of a pale green colour and soluble in carbonate of ammonia.

Peroxide or *sesquioxide of nickel*, Ni_2O_3, is obtained as a black powder, by exposing the hydrated protoxide suspended in water to a stream of chlorine gas. It

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* Berzelius, Traité, tom. i., p. 486; see also pp. 469–470, of this volume.

does not combine with acids, and in other respects resembles sesquioxide of cobalt.

Besides a *protosulphide*, NiS, a *subsulphide of nickel*, Ni_2S, is formed, like that of manganese, by decomposing the ignited sulphate of nickel with hydrogen. A *bisulphide of nickel* also exists in combination as a constituent of the mineral nickel-glance, $NiS_2.NiAs$.

Chloride of nickel $NiCl$, forms a solution of an emerald-green colour, and yields by evaporation a hydrated salt of the same colour, which becomes yellow when deprived of its water of crystallization. Chloride of nickel, sublimed at a high temperature without access of air, forms golden scales which dissolve with difficulty.

Sulphate of nickel, crystallizes from a strong solution in slender green prisms, isomorphous with Epsom salt, of which the composition is $NiO.SO_3 + 7HO$. At a higher temperature, it crystallizes with 6 eq. of water $NiO.SO_3 + 6HO$, like the magnesia and cobalt salts, and in the same form. Mitscherlich made the singular observation, that when the crystals containing 7 eq. of water are exposed, in a close glass vessel, to a day of sunshine, or kept for some time in a temperate place, they change their form, becoming a mass of small crystals, of which the form is the regular octohedron. The original crystals become opaque from this change, but lose none of their combined water. Sulphate of nickel forms the usual double salts with the sulphates of potash and ammonia.

Nickel also forms ammonio-compounds analogous to the ammonio-cobalt salts; *e.g. the ammonio-chloride* $= 3NH_3.NiCl = N\overbrace{H\,Am_2Ni}.Cl$; *ammonio-sulphate* $= 5NH_3.NiSO_4 = N\overbrace{H\,Am_2Ni}.SO^4$, &c.

The useful white *alloy of nickel*, German silver or *packfong*, is formed by fusing together 100 parts of copper, 60 of zinc, and 40 of nickel.

ESTIMATION OF NICKEL, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Nickel is best precipitated from its solutions by caustic potash, which throws down an apple-green precipitate of the hydrated protoxide, and if the liquid be heated, leaves not a trace of nickel in the solution. The precipitate must be washed with hot water, dried, ignited, and weighed; it then consists of pure protoxide of nickel, containing 78·57 per cent. of the metal.

In separating nickel from other metals, it is often necessary to precipitate it by sulphide of ammonium; this precipitation is attended with difficulties, because the sulphide of nickel is somewhat soluble in the alkaline sulphide. To make the precipitation as complete as possible, Rose directs that the solution be diluted with a considerable quantity of water, and then treated with sulphide of ammonium, as nearly colourless as it can be obtained, avoiding a large excess of the precipitant and likewise an excess of ammonia; the glass is then to be covered up with filtering paper, and left in a warm place. Under these circumstances, the excess of sulphide of ammonium is decomposed by the oxygen and carbonic acid of the air, without risk of the sulphide of nickel being oxidized. As soon as the supernatant liquid has lost its brown colour, the precipitate is collected on a filter and washed, as quickly as possible, with water containing a little sulphide of ammonium. It must then be dissolved in nitro-hydrochloric acid, and the nickel precipitated by potash as above.

The methods of separating nickel from all the preceding metals except cobalt, are the same as those given for cobalt (p. 466).

The separation of nickel from cobalt itself is difficult. The best method is perhaps that given by H. Rose,* depending on the fact that protoxide of cobalt in

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* Handbuch der Analytischen Chemie (Berlin, 1851), ii. 164.

solution is converted by chlorine into sesquioxide, whereas with nickel this change does not take place. The metals or their oxides being dissolved in excess of hydrochloric acid, the solution is diluted with a large quantity of water, about a pound of water to a gramme of the metals or their oxides. Chlorine gas is then passed through the solution for several hours, till in fact the space above the liquid becomes permanently filled with the gas; carbonate of baryta is then added in excess, the whole left to stand for 12 or 18 hours, and shaken up from time to time. The precipitate, consisting of sesquioxide of cobalt and carbonate of baryta, is then collected on a filter, and washed with cold water. The filtered liquid, which has a pure green colour, contains all the nickel without a trace of cobalt. The precipitate is boiled with hydrochloric acid to convert the sesquioxide of cobalt into protoxide, and dissolve it together with the baryta; the latter is then precipitated by sulphuric acid, and the cobalt from the filtrate by potash. The nickel is also precipitated by potash after the removal of any baryta that the solution may contain by sulphuric acid. This method, if properly executed, gives very exact results. The chief precautions to be attended to, are to add a large excess of chlorine, and not to filter too soon, because the precipitation of sesquioxide of cobalt by carbonate of baryta takes a long time.

Liebig has given several methods of separating these two metals, founded on the difference of their reactions with cyanide of potassium. 1. The oxides of the two metals are treated with hydrocyanic acid and then with potash, and the liquid warmed till the whole is dissolved (pure cyanide of potassium, free from cyanate may also be used as the solvent). The reddish-yellow solution is boiled to expel free hydrocyanic acid, whereupon the cobaltocyanide of potassium (K_2CoCy_3), formed in the cold, is converted into cobalticyanide ($K_3Co_2Cy_6$), while the nickel remains in the form of cyanide of nickel and potassium ($KNiCy_2$). Pure and finely-divided red oxide of mercury is then added to the solution while yet warm, whereby the whole of the nickel is precipitated partly as oxide, partly as cyanide, the mercury taking its place in the solution. The precipitate contains all the nickel, together with excess of mercuric oxide; after washing and ignition, it yields pure oxide of nickel. The filtered solution contains all the cobalt in the form of cobalticyanide of potassium. It is supersaturated with acetic acid, boiled with sulphate of copper, which precipitates the cobalt in the form of cobalticyanide of copper ($Cu_3Co_2Cy_6 . 7HO$), and the precipitate retained in the liquid at a boiling-heat till it has lost its glutinous character. It is then washed, dried, and ignited, dissolved in hydrochloric acid mixed with a little nitric acid, the copper precipitated by hydrosulphuric acid, and the filtrate, after boiling for a minute to expe- the excess of that gas, mixed with boiling caustic potash to precipitate the cobalt.* —2. Instead of adding the oxide of mercury, the solution containing the mixed cyanides may, after cooling, be supersaturated with chlorine, the precipitate of cyanide of nickel thereby produced being continually redissolved by caustic potash or soda. The chlorine produces no change on the cobalticyanide of potassium, but decomposes the nickel-compound, the whole of the nickel being ultimately precipitated in the form of black sesquioxide.†

Liebig's first method‡ which consisted in treating the solution of the mixed cyanides with excess of hydrochloric or sulphuric acid, whereby the nickel was precipitated as cobalticyanide of nickel, leaving a solution of pure cobalticyanide of potassium, has been found, both by himself and others, not to give perfectly satisfactory results. The method by oxalic acid (p. 466), and the precipitation of nickel from an ammoniacal solution of the two metals by potash (p. 467) are not sufficiently accurate for quantitative analysis.

F. Claudet proposes to separate cobalt from nickel and other metals in the form of the ammonio-compound described on page 465, that compound being very

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* Ann. Ch. Pharm. lxv. 244.

† Ann. Ch. Pharm. lxxxvii. 128.

‡ Ibid. xli. 291.

insoluble, while corresponding compounds of the other metals do not appear to be formed under the same circumstances.

The separation of cobalt from nickel (also from zinc and the previously described metals) may likewise be effected by means of St. Evre's yellow compound, which is regarded by A. Stromeyer as a nitrite of cobaltic oxide and potash (p. 462). The solution containing the mixed metals is diluted with water till about 300 parts of water are present to 1 part of protoxide of cobalt; a somewhat concentrated solution of nitrite of potash* then added, and a sufficient quantity of acetic acid to redissolve any precipitated carbonates; and the solution left to stand for 12 to 24 hours in a covered vessel, then filtered and washed, first with acetate of potash, afterwards with alcohol. The precipitate contains all the cobalt in the form of the above-mentioned salts, and none of the other metals.†

SECTION V.

ZINC.

32·52; Zn. *or Eq.* 406·6.

The principal ores of zinc are *calamine*, or the carbonate, a pulverulent mineral generally of a reddish or flesh colour, and *zinc-blende*, a massive mineral of an adamantine lustre, and often black. The oxide, from the carbonate or from the calcined sulphide, is mixed with about ¾ of its weight of carbonaceous matter, and heated to a low white heat in retorts, or similar vessels of earthenware or iron. The zinc is then reduced and volatilized, and condenses in the colder part of the apparatus.

In Silesia, the mixture of zinc-oxide and charcoal, or coke, is heated in muffles, (fig. 189) 3 feet long and 18 inches high, six of which are laid in one furnace (fig. 190), three side by side. The evolved mixture of carbonic oxide and zinc-vapour passes from the upper and fore part of the muffles M, through a knee-shaped channel, *b c d*, and the zinc condenses therein and drops down from the lower aperture *d* into the reservoirs *t* (fig. 190) placed beneath.

Fig. 189.

Part of the zinc-vapour, and likewise some cadmium-vapour, escapes uncondensed, together with the carbonic oxide gas, and burns in the air, producing the substance called *Silesian zinc-flowers*. Silesia furnishes the greater part of the zinc used in the arts.

In Belgium, the reduction is performed in earthenware tubes, laid side by side; and the zinc as it condenses in the fore part of these tubes, is scraped out from time to time in the liquid state.

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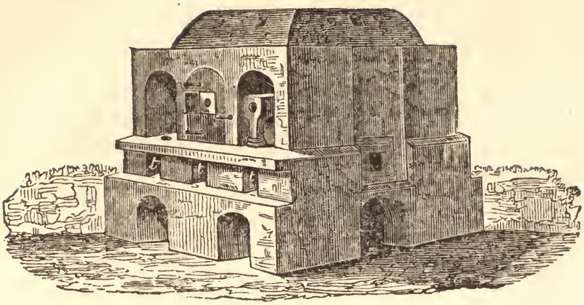
* The nitrite of potash is prepared by fusing 1 part of nitre in contact with 2 parts of metallic lead, first at a low and then at a bright-red heat, exhausting the cooled mass with water, precipitating a small quantity of lead by carbonic acid, and then by sulphide of ammonium, evaporating to dryness, and heating to the melting-point to decompose any hyposulphite of potash that may have been formed.

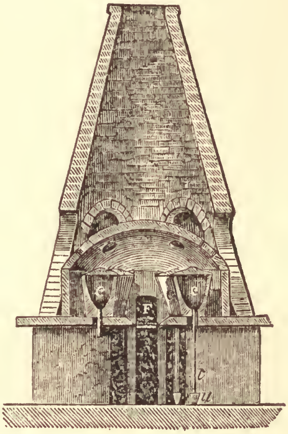
† A. Stromeyer, Ann. Ch. Pharm. xcvi. p. 218; see also Liebig and Kopp's Jahresbericht, 1854, p. 357.

FIG. 190.



In England, a number of cast-iron pots are arranged in a circle in the furnace (fig. 191.). Through the bottom of each of these pots, there passes an iron tube *t t′*, which is continued downwards through an aperture in the bottom of the furnace. The upper end of the tube is stopped with a plug of wood, which is charred during the operation, and becomes sufficiently porous to allow the passage of the zinc-vapour, but at the same time prevents the solid matter from falling through. Each pot is fitted with a cover well luted with clay. The fire-place F, is in the middle. The distilled zinc condenses in the tubes *t t′*, and falls in drops into a receiver *u*, placed beneath. This process is called *destillatio per descensum.*

FIG. 191.



Zinc may be purified by a second distillation in a porcelain retort; but the first portions of that metal which come over should be rejected, as they generally contain cadmium and arsenic.

Zinc is a white metal, with a shade of blue, capable of being polished and then assuming a bright metallic lustre. It is usually brittle, and its fracture exhibits a crystalline structure. But zinc, if pure, may be hammered into thin leaves, at the usual temperature; and commercial zinc, which is impure and brittle at a low temperature, acquires the same malleability between 210° and 300°: it may then be laminated; and the metal is now consumed in the form of sheet zinc for a variety of useful purposes. At 400° it again becomes brittle, and may be reduced to powder in a mortar of that temperature. The density of cast zinc is 6·862, but it may be increased by forging to 7·21. Its point of fusion is 773° (Daniell). At a red heat, zinc rises in vapour and takes fire in the air, burning with a white flame like that of phosphorus; the white oxide produced is carried up mechanically in the air, although itself a fixed substance. Laminated zinc is a valuable substance, from its little disposition to undergo oxidation. When exposed to air or placed in water, its surface becomes covered with a grey film of suboxide, which does not increase; this film is better calculated to resist both the mechanical and chemical effects of other bodies than the metal itself, and preserves it. Zinc dissolves with facility in dilute hydrochloric, sulphuric and other hydrated acids, by substitution for hydrogen. In contact with iron, it protects the latter from oxidation in any saline fluid.

Zinc appears to form three oxides, the suboxide above referred to, the protoxide, and a peroxide, which last is produced when the hydrated protoxide is acted upon by a solution of peroxide of hydrogen; but of these, the first and last have not been studied, and the protoxide is, therefore, the only well known oxide of zinc.

Protoxide of zinc; ZnO; 40·52 *or* 506·6.—This oxide may be obtained, in the form of an anhydrous white powder, by the combustion of the metal in a stoneware crucible, or as a white hydrate, by precipitation from its salts by an alkali. It is of a yellow colour at high temperatures, but becomes colourless again on cooling. By the oxidation of zinc in air and water, without access of carbonic acid, a hydrate, $3ZnO + HO$, has been obtained in crystalline needles (Mitscherlich).

Oxide of zinc combines with acids and forms salts, which are colourless, like those of magnesia. *Caustic alkalies* form with zinc-salts a white gelatinous precipitate of the hydrated oxide, soluble in excess of the alkali. *Carbonate of potash* or *soda* throws down white carbonate of zinc, insoluble in excess; *carbonate of ammonia*, the same precipitate, soluble in excess. *Ferrocyanide of potassium*, and the *alkaline phosphates* and *arseniates*, also form white precipitates. Zinc-salts containing a strong acid in excess, are not affected by hydrosulphuric acid, but give a white hydrated sulphide with *alkaline sulphides.* A solution of acetate of zinc is readily decomposed by hydrosulphuric acid.

The native *sulphide of zinc*, or *zinc-blende*, ZnS, crystallizes in octohedrons. Its colour is variable, being sometimes yellow, red, brown, or black.

Chloride of zinc, $ZnCl$, is produced by the combustion of zinc in chlorine, and by dissolving the metal in hydrochloric acid. It is fusible at 212°, volatile at a red heat, and perhaps the most deliquescent of salts. *Chloride of zinc-ammonium*, $NH_3Zn.Cl$, is obtained, according to Ritthausen, in white prismatic crystals, when zinc and copper, or zinc and silver, are placed in contact in a solution of sal-ammoniac, or by the action of zinc on a solution of sal-ammoniac containing chloride of copper.

Iodide of zinc is formed by digesting iodine, zinc, and water together, and resembles the chloride. The compound $ZnI.2NH_3$, or $\overbrace{NH_2(NH_4)}Zn.I$, forms crystals belonging to the rhombic system (Rammelsberg).

The neutral *carbonate of zinc* forms the ore called calamine. When precipitated by an alkaline carbonate, the salts of zinc, like those of magnesia, yield the neutral carbonate in combination with hydrated oxide, $2(ZnO.CO_2)+3(ZnO.HO)$. The mineral substance, *zinc-bloom*, is of the same composition. Precipitated in the cold, the carbonate is $ZnO.CO_2+2(ZnO.HO)$, but is contaminated with sulphate of soda (Mitscherlich).

Sulphate of zinc, White vitriol, $ZnO.SO_3+7HO$.—This salt is formed by the oxidation of the native sulphide at high temperatures, or by dissolving the metal in dilute sulphuric acid. It crystallizes in colourless prismatic crystals, containing 7 eq. of water, the form of which is a right rhombic prism. This, like all the other magnesian sulphates, gives up 6 eq. of its water at about 212°, while the seventh or constitutional equivalent requires a heat of 400° to expel it. The crystals are soluble in 2½ times their weight of water, at the usual temperature, and fuse in their water of crystallization when heated. The salt also crystallizes above 86°, with 6 eq. of water, in oblique rhombic prisms (Mitscherlich.) According to Kühn, another hydrate is formed and precipitated as a white powder containing 2 eq. of water, when a concentrated solution of sulphate of zinc is mixed with oil of vitriol. Sulphate of zinc forms the usual double salt with sulphate of potash, $ZnO.SO_3+KO.SO_3+6HO$. The double sulphate of zinc and soda contains 4 atoms of water, $ZnO.SO_3+NaO.SO_3+4HO$. It is formed by a singular decomposition (p. 183). When a solution of the sulphate is mixed with a quantity of alkali less than sufficient for complete precipitation, a *subsulphate of zinc* precipitates, which, according to the analyses of several chemists, contains 4 eq. of oxide of zinc to 1 eq. of sulphuric acid, besides water. A concentrated solution of sulphate of zinc dissolves the preceding subsalt, and, when saturated, contains a compound of 1 eq. of acid and 2 eq. of base, according to Schindler, and does not crystallize. From this solution, Schindler obtained the former insoluble subsalt with two different proportions of water, in long crystalline needles, containing 10HO, by spontaneous evaporation of the solution, and in brilliant crystalline plates containing 2HO, which were deposited on boiling the solution. By diluting the same solution with a large quantity of water, he also obtained another subsalt, as a light bulky precipitate, which contained 1 eq. of acid, 8 eq. of oxide of zinc, and 2 eq. of water. The insoluble matter, which precipitates when sulphate of zinc-ammonium $(NH_3Zn)O.SO_3$ is thrown into water, is considered by Kane as a third subsulphate of zinc, containing 1 eq. of acid, 6 eq. of oxide of zinc, and 10 eq. of water. All these subsulphates afford neutral sulphate of zinc to water, after being heated to redness; so that, whatever their constitution may be when hydrated, it is certainly different from what it is in their anhydrous condition.

Nitrate of zinc, $ZnO.NO_5+6HO$, is very soluble in water, and moderately deliquescent.

Phosphate of zinc, $ZnO_2.HO.PO_5 + 2HO$, is obtained in minute silvery plates, which are nearly insoluble, on mixing dilute solutions of phosphate of soda and sulphate of zinc.

Silicate of zinc is found as a crystalline mineral, which has received the name of the electrical oxide of zinc, because it acquires, like the tourmalin, a high degree of electrical polarity when heated. It contains water, and may be represented by the formula $2(3ZnO.SiO_3)+3HO$.

The most important *alloys of zinc* are those with copper, which form the varieties of brass. Zinc also combines readily with iron, and is contaminated by that metal, when fused in an iron crucible.

ESTIMATION OF ZINC, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Zinc is precipitated from its solutions by carbonate of soda, which, when added in excess and boiled with the solution, throws down carbonate of zinc. It is best, however, to pour the zinc-solution into the hot solution of the alkaline carbonate, because, in that case, we may be sure of not forming a basic salt. If the zinc-solution contains ammoniacal salts, it must be boiled with a quantity of carbonate of soda sufficient to decompose those salts; then evaporated to dryness; the residue treated with a large quantity of water to dissolve out the soluble salts; and the carbonate of zinc collected on a filter and well washed with hot water. The evaporation should be conducted as quickly as possible. The carbonate of zinc, when dried and ignited, yields oxide of zinc containing 80·26 per cent. of the metal.

In separating zinc from other metals, it is often necessary to precipitate by sulphide of ammonium. If the solution is acid, it must be previously neutralized by ammonia. The precipitate must not be thrown on the filter immediately, but left to settle down completely, after which the clear liquid must first be passed through the filter, and then the precipitate thrown on it. If this precaution be neglected, the sulphide of zinc will stop up the pores of the filter. The precipitate is washed with water containing a little sulphide of ammonium; then dissolved in hydrochloric acid; the solution boiled to drive off the hydrosulphuric acid; and the zinc precipitated by carbonate of soda as above.

Zinc is separated from the *alkalies* and *alkaline earths* (baryta, strontia, and lime) by means of sulphide of ammonium. In the case of the alkaline earths. however, great care must be taken to prevent the ammoniacal liquid from absorbing carbonic acid from the air, as that would occasion a precipitation of the earth in the form of carbonate. For this purpose, the filtration must be effected as quickly as possible, and the liquid well protected from the air. The separation of zinc from *baryta* may also be effected by sulphuric acid, and from *lime* by oxalate of ammonia.

From *magnesia*, zinc may be separated by sulphide of ammonium, a sufficient quantity of chloride of ammonium being previously added to prevent the precipitation of the magnesia. Or the separation may be effected by converting the zinc and magnesia into acetates, and precipitating the zinc as sulphide by hydrosulphuric acid.

The separation of zinc from *alumina* and *glucina* may also be effected by converting the two bases into acetates and precipitating the zinc by hydrosulphuric acid; or by dissolving in potash, and precipitating the zinc by hydrosulphuric acid; but the former method is to be preferred.

The conversion into acetates and precipitation by hydrosulphuric acid likewise serves to separate zinc from *zirconia*, *yttria*, *thorina*, and *manganese.* The separation from manganese may also be effected by converting the two metals into chlorides, passing chlorine gas through the solution to convert the manganese into bioxide, and completing the precipitation of the latter by carbonate of baryta.

From *iron*, zinc may be separated by ammonia, or better by succinate of ammonia, the same precautions being used as in the separation of iron from manganese by the same method (p. 458). The iron (in the state of sesquioxide) may also be precipitated by carbonate of lime or carbonate of baryta.

From *cobalt* and *nickel*, zinc is separated by dissolving the oxides of both metals in *excess* of acetic acid, and precipitating the zinc by hydrosulphuric acid. Nickel and cobalt are completely precipitated by hydrosulphuric acid from the neutral solutions of their acetates, but not when a considerable excess of acetic acid is present. But in separating zinc from cobalt and nickel in this manner, a small quantity of the latter metals is generally precipitated with the zinc towards the end of the process, the precipitate then becoming greyish black. In that case it must be redissolved in hydrochloric acid, the chlorides converted into acetates, and the precipitation repeated. Another method of separation is to convert the metals into chlorides, and ignite the dry chlorides in a stream of hydrogen gas: the nickel or cobalt is then reduced to the metallic state, while the chloride of zinc remains unaltered, and may be dissolved out by water. (For the separation of cobalt from zinc, see also p. 470.)

In precipitating zinc from its acetic acid solution by hydrosulphuric acid, it is necessary that the solution be quite free from inorganic acids, which would interfere with the precipitation. This may be effected either by precipitating the metals with carbonate of soda, washing the precipitate and dissolving it in acetic acid, or by boiling the solution with excess of sulphuric acid to drive off the inorganic acids (if volatile) and decomposing the sulphate with acetate of baryta.

SECTION VI.

CADMIUM.

Eq. 55·74 *or* 696·77; Cd.

This metal is frequently found in small quantity, associated with zinc, and derives the name cadmium, applied to it by Stromeyer, from *cadmia fossilis*, a denomination by which the common ore of zinc was formerly designated. In the process of reducing ores of zinc, the cadmium which they contain comes over among the first products of distillation, owing to its greater volatility. It may be separated from zinc, in an acid solution, by hydrosulphuric acid, which throws down cadmium as a yellow sulphide. This sulphide dissolves in concentrated hydrochloric acid, affording the chloride of cadmium, from which the carbonate may be precipitated by an excess of carbonate of ammonia. Carbonate of cadmium is converted by ignition into the oxide; and the latter yields the metal when mixed with one-tenth of its weight of pounded coal, and distilled in a glass or porcelain retort, at a low red heat.

Cadmium is a white metal, like tin, very ductile and malleable. It fuses considerably under a red heat, and is nearly as volatile as mercury. The density of cadmium, cast in a mould, is 8·604, after being hammered, 8·6944. Cadmium may be dissolved in the more powerful acids, by substitution for hydrogen, with the aid of heat; but nitric acid is its proper solvent.

Oxide of cadmium, CdO; 63·74 *or* 796·77.—The only known oxide of cadmium is obtained by the combustion of the metal, or by the ignition of its carbonate, as a powder of an orange colour, or as a white hydrate by precipitation from its salts by an alkali. Its density, in the anhydrous condition, is 8·183 (Herapath). By igniting the nitrate, the oxide is obtained in microscopic octohedrons, which are dark bluish black by reflected, and dark brown with a tinge of violet by transmitted light (Schüler). This oxide is soluble in ammonia, but not in its carbonate (differing in the last property from zinc and copper) nor in the fixed alkalies. Its salts are white, and greatly resemble those of zinc. They are precipitated of a fine yellow colour by hydrosulphuric acid.

Sulphide of cadmium is distinguished from sulphide of arsenic, which it resembles in colour, by being insoluble in potash and in sulphide of ammonium, and by sustaining a red heat without subliming. A crystalline sulphide is obtained by fusing 1 part of the precipitated sulphide with 5 parts of carbonate of potash and 5 parts of sulphur; or by passing dry hydrosulphuric acid gas over strongly-heated chloride of cadmium.

Chloride of cadmium forms a crystalline hydrate, containing $CdCl + 2HO$. It also forms crystalline compounds with the chlorides of ammonium, potassium, sodium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. A solution of chloride of cadmium, mixed with excess of ammonia, yields by spontaneous evaporation the compound NH_2CdCl (C. v. Hauer).

The same ammoniacal solution treated with excess of hydrochloric acid deposits crystalline crusts, which, according to Schüler, contain $CdCl.3NH_3$ or $\overgroup{NH(NH_4)_2Cd}.Cl$. Sulphurous acid gas passed through the ammoniacal solution throws down a white crystalline precipitate containing $CdO.SO_2 + NH_4O.SO_2$ (Schüler.)

Iodide of cadmium forms a crystalline compound with water.

Bromide of cadmium mixed in equivalent quantity with bromide of potassium in solution, yields crystals, first of $2CdBr.KBr+2HO$, afterwards of $CdBr.2KBr$ (C. v. Hauer).

Sulphate of cadmium forms efflorescent crystals containing $CdO.SO_3 + 4HO$ (Stromeyer). According to Kühn and Von Hauer, an acid solution of the salt concentrated at the boiling heat, deposits nodular crystals, which contain $CdO.SO_3 + HO$, and give off their water at 212°. The crystals obtained by evaporation at ordinary temperatures contain $3(CdO.SO_3) + 8HO$, give off nearly 3 eq. water at 212°, and the rest at a low red heat (C. v. Hauer). Sulphate of cadmium forms with sulphate of potash the compound $CdO.SO_3 + KO.SO_3 + 6HO$, and similar double salts with the sulphates of soda and ammonia.

Several definite *alloys of cadmium* have been formed. At a red heat, 100 parts of platinum retain 117·3 parts of cadmium, giving a compound $= Cd_2Pt$: 100 parts of copper retain, at a red heat, 82 2 of cadmium, which approaches nearly to the proportion of $CdCu_2$. Cadmium forms an amalgam with mercury, which crystallizes in octohedrons, and consists of 21·74 parts of cadmium, and 78·26 of mercury, $CdHg_2$.

Estimation of cadmium, and method of separating it from the preceding metals.—Cadmium is best precipitated from its solutions by carbonate of soda; it is thereby obtained as a carbonate, which by ignition yields the brown oxide containing 87·45 per cent. of the metal.

From all the preceding metals cadmium may be separated by hydrosulphuric acid; the sulphide of cadmium being then dissolved by nitric acid, and the metal precipitated by carbonate of soda as above.

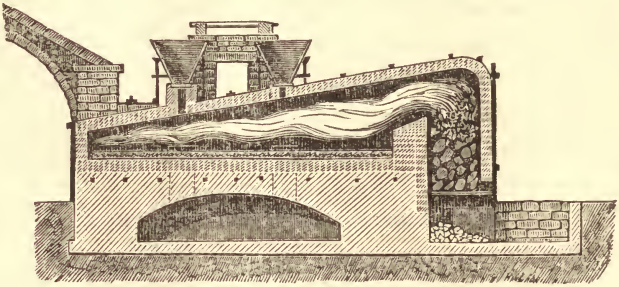
SECTION VII.

COPPER.

Eq. 31·66 *or* 395·7; Cu (*cuprum*).

Copper, if not the most abundant, is certainly one of the most generally diffused of the metals. Its ores are often accompanied by metallic copper, crystallized in cubes or octohedrons. Very large masses of native copper have been found near Lake Superior in North America, one of which weighed 2200 pounds; in the Cliff mine, on the Eagle river, a mass has been found weighing 50 tons. Native copper is also found in considerable quantities in the decomposed basalt of Rheinbreitenbach, near Recsk in Hungary, and near Harlech, North Wales. The richest mines of Britain are those in Cornwall and Anglesea. The common ore of this metal is *copper pyrites*, a compound of subsulphide of copper and sesquisulphide of iron, or a sulphur-salt, $CuS+Fe_2S_3$, but in which the two sulphides are also found in other proportions, and which also contains an admixture of the bisulphide of iron. Few metallurgic processes require more skill and attention than the extraction of copper from this ore. The ore is first roasted at a high temperature in a reverberatory or flame-furnace, (fig. 192), whereby the sulphide of iron is in great part converted into oxide, while the sulphide of copper remains unaltered. The product of this operation is then strongly heated with silicious sand, which combines with the oxide of iron, forming a fusible slag, and separates from the heavier copper compound. This operation is performed in a reverberatory furnace similar to the former, but of smaller dimensions. These processes are several times repeated, whereby the quantity of iron is continually diminished, and the sulphide of copper begins to decompose, giving it up its sulphur and absorbing oxygen; the temperature is then raised high enough to reduce the resulting oxide by the aid of carbonaceous matter. The *coarse copper* thus obtained, containing from 80 to 90 per cent. of copper, is then melted under the action of a strong blast of air, to complete the expulsion of volatile matter, and the copper is partially oxidized. Lastly, to free it from oxide, which renders it brittle, it is again melted with its surface well covered with charcoal, and a pole of birchwood is thrust into it; this causes considerable ebullition, the oxide being reduced by the carbonaceous matter, and carbonic acid escaping. Samples of the

FIG. 192.



metal are taken out from time to time, and tested by the hammer, the process being discontinued as soon as the right degree of toughness is attained. If the *poling* is continued too long, the copper takes up carbon, and then becomes even more brittle than in its former oxidized state: it is then said to be *over-poled*, and must be again melted in contact with the air to burn away the carbon.*

Copper is the only metal of a red colour. The crystals of native copper, and of that obtained in the humid way by precipitation with iron, belong to the regular system; but the crystals which form in the cooling of melted copper were found by Seebeck to be rhomboïdal, and to have a different place in the thermo-electric series from the other crystals. The density of copper when cast is about 8·83, and when laminated or forged 8·95 (Berzelius). It is less fusible than silver, but more so than gold, its point of fusion being 1996° (Daniell). It is one of the most highly malleable metals, and in tenacity is inferior only to iron. It has much less affinity for oxygen than iron, and decomposes water only at a bright red heat, and to a small extent. In damp air, it acquires a green coating of subcarbonate of copper, and its oxidation is remarkably promoted by the presence of acids. The weaker acids, such as acetic, have no effect upon copper, unless with the concurrence of the oxygen of the air, when the copper rapidly combines with that oxygen, and a salt of the acid is formed. Copper scarcely decomposes the hydrated acids by displacing hydrogen; when boiled in hydrochloric acid, it disengages only the smallest traces of that gas. But hydrogen does not precipitate metallic copper from solution. Copper acts violently on nitric acid, occasioning its decomposition, with evolution of nitric oxide, and dissolving as a nitrate.

Dioxide of copper, Red oxide of copper, Cuprous oxide, Cu_2O; 71·32 or 891·4.—This degree of oxidation is better marked in copper than in any other metal of the magnesian class. The dioxide of copper is found native in octohedral crystals, and may be prepared artificially by heating to redness, in a covered crucible, a mixture of 5 parts of the black oxide of copper with 4 parts of copper-filings. It is a reddish-brown powder, which undergoes no change in the air. The surface of vessels of polished copper is often converted into red oxide, or bronzed, to enable them to resist the action of air and moisture: this is done by covering them with a paste of sesquioxide of iron, heating to a certain point, and afterwards cleaning them, to remove the oxide of iron; or otherwise, by means of a boiling solution of acetate of copper.

Dilute acids decompose red oxide of copper, dissolving the protoxide, and leaving metallic copper. Undiluted hydrochloric acid dissolves the red oxide, without decomposition, or rather forms a corresponding chloride of copper, Cu_2Cl, which is soluble in hydrochloric acid. The hydrated alkalies precipitate hydrated cuprous oxide from that solution, of a lively yellow colour, which changes rapidly in air from absorption of oxygen.

Cuprous oxide is also formed when copper is placed in a dilute solution of ammonia containing air, and is dissolved by the alkali. If the ammonia has been corked up in a bottle with copper for some time, the liquid is colourless; but on pouring it out in a thin stream, it immediately becomes blue, by absorbing oxygen. The liquid may be again deprived of colour by returning it to the bottle, and closing it up, in contact with the metal. Cuprous oxide is also readily obtained by the reducing action of glucose (grape-sugar) on the protoxide or its salts. When a solution of 1 part of common sulphate of copper and 1 part of glucose is mixed with a sufficient quantity of caustic potash or soda to redissolve the precipitate first formed, and the liquid gently warmed, cuprous oxide is abundantly precipitated in the form of a yellowish-red crystalline powder. Cane-sugar produces the same effects, but more slowly, apparently because it must first be converted into glucose.

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* A minute account of the process of copper-smelting as practised at Swansea, has lately been given by Mr. Napier in the "Philosophical Magazine," 4th Series, vols. iv. and v.

Compounds have been obtained of cuprous-oxide with several acids, particularly with sulphurous acid, the sulphite forming a double salt with sulphite of potash, $Cu_2O.SO_2 + 2(KO.SO_2)$ (Muspratt); also with hyposulphurous, sulphuric, carbonic and acetic acids. When fused with vitreous matter, cuprous oxide gives a beautiful ruby-red glass; but it is difficult to prevent the cuprous oxide from absorbing oxygen, in which case the glass becomes green.

Hydride of copper, Cuprous hydride, Cu_2H.—When a solution of cupricsulphate and hypophosphorous acid is heated not above 158°, this compound is deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and when treated with hydrochloric acid, is converted into dichloride of copper, with evolution of a double quantity of hydrogen, the acid in fact giving up its hydrogen as well as the copper compound (Wurtz):

$$Cu_2H + HCl = Cu_2Cl + HH.$$

This action is very remarkable, inasmuch as metallic copper is scarcely acted upon by hydrochloric acid. It appears to arise from the two atoms of hydrogen contained in the acid and the hydride being in opposite states, the former being basylous or positive, the latter chlorous or negative, and so disposed to *combine together*, just as the hydrogen of the hydrochloric acid combines under similar circumstances with the oxygen of the compound Cu_2O. The reduction of certain metallic oxides by peroxide of hydrogen affords another example of the same kind of action.

Disulphide of copper, Cuprous sulphide, Cu_2S, forms the mineral *copper-glance*, and is also a constituent of copper pyrites. It is a powerful sulphur-base. Copper-filings, mixed with half their weight of sulphur, unite, when heated, with intense ignition, and form this disulphide.

Dichloride of Copper, Cuprous chloride, Cu_2Cl, may be prepared by heating copper-filings with twice their weight of corrosive sublimate. It was obtained by Mitscherlich in tetrahedrons, by dissolving in hydrochloric acid the dichloride of copper formed on mixing solutions of the protochlorides of copper and tin, and allowing the concentrated solution to cool. Dichloride of copper so prepared is white, insoluble in water, soluble in hydrochloric acid, but precipitated by dilution. It is dissolved by a boiling solution of chloride of potassium, and the resulting solution, if allowed to cool in a close vessel, yields large octohedral crystals of a double chloride: $Cu_2Cl.2KCl$; they are anhydrous. It is remarkable that the forms of this double salt, and of both its constituents, all belong to the regular system.*

When finely-divided metallic copper is boiled in a saturated solution of sal-ammoniac, ammonia is evolved and a white salt formed, which crystallizes in rhombic dodecahedrons: it contains $NH_3.Cu_2Cl$, and may be regarded as a dichloride of copper and cuprammonium $\left.\begin{matrix}NH_3Cu\\Cu\end{matrix}\right\}Cl$. A solution of this salt exposed to the air yields blue crystals of the compound $NH_3.Cu_2Cl + NH_3CuCl + HO$; and the mother-liquor, after further exposure to the air, contains the salt $NH_3 . CuCl + NH_4Cl$, which at a lower temperature crystallizes in large cubes (Ritthausen).

Diniodide of Copper, Cuprous iodide, Cu_2I, is a white insoluble precipitate, obtained on mixing a solution of 1 part of sulphate of copper and 2¼ parts of protosulphate of iron, with a solution of iodide of potassium.

Dicyanide of copper, Cuprous cyanide, Cu_2Cy. — Obtained as a white curdy precipitate on adding hydrocyanic acid or cyanide of potassium to a solution of dichloride of copper in hydrochloric acid, or to a solution of protochloride of copper mixed with sulphurous acid. It forms a colourless solution with ammonia, and a yellow solution with strong hydrochloric acid, from which it is precipitated by potash

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* Mitscherlich in Poggendorff's Annalen, xlix. 401, 1840.

Dicyanide of copper unites with the cyanides of the alkali and earth-metals, and with the cyanides of manganese, iron, zinc, cadmium, lead, tin, uranium, and silver, forming double salts, some of which have the composition $MCy.Cu_2Cy$, others $3MCy.Cu_2Cy$ (the symbol M denoting a metal).

Cuproso-cupric cyanide, $Cu_2Cy . CuCy$, is obtained as a green hydrate by adding hydrocyanic acid or cuproso-potassic cyanide, $KCy.Cu_2Cy$, to sulphate of copper. It forms three compounds with ammonia, viz., $NH_3.Cu_3Cy_2.HO$, obtained by adding cyanide of ammonium to a protosalt of copper, and the compounds $2NH_3.Cu_3Cy_2$ and $3NH_3.Cu_3Cy_2$, formed by the action of ammonia on the first compound.

Cuprous hyposulphite, $Cu_2O.3S_2O_2 + 2HO$, separates in microscopic needles, having a golden lustre, on adding a saturated solution of hyposulphite of soda to a concentrated solution of cupric sulphite, till a deep yellow colour is produced. It dissolves in aqueous sal-ammoniac, and the solution deposits the compound $Cu_2O.3S_2O_2 + NH_3CuCl + HO$. (C. v. Hauer).

Cuprous sulphite is said by some chemists to be obtained in a definite state by the action of sulphurous acid on cupric oxide; but according to Rammelsberg and Péan de St. Gilles, it exists only in combination with cupric sulphite, forming the compound $Cu_2O.SO_2 + CuO.SO_2$, which crystallizes with 3 and 5 eq. of water, —and with the sulphites of the alkalies. By treating dichloride of copper with excess of sulphite of ammonia, prismatic crystals are formed containing $Cu_2O.SO_2 + 7(NH_4O.SO_2) + 10$ Aq ; and by saturating the solution of this salt with sulphurous acid, the salt $Cu_2O.S_2O_2 + NH_4O.SO_3$ is obtained. A concentrated solution of sulphite of ammonia and cupric sulphate saturated with sulphurous acid gas, yields light green crystals containing $(Cu_2O.SO_2 + NH_4O . SO_2) + (Cu_2O . SO_2 + CuO . SO_2) + 5$ aq. Corresponding double salts are formed by the sulphites of potash and soda, but they are very unstable.

Protoxide of copper, Black oxide of Copper, Cupric oxide, CuO; 495·7 or 39·66. — The base of the ordinary salts of copper, or cupric salts. It is formed by the oxidation of copper at a red heat, but is generally prepared by igniting the nitrate of copper. It is black like charcoal, and fuses at a high temperature. This oxide is remarkable for the facility with which it is reduced, at a low red heat, by hydrogen and carbon, which it converts into water and carbonic acid. It is this property which recommends oxide of copper for the combustion of organic substances, in close vessels, by which their ultimate analysis is effected.

Oxide of copper is a powerful base. Its salts, the *cupric* salts, are generally blue or green, when hydrated, but white when anhydrous. Although neutral in composition, they have a strong acid reaction. They are poisonous; but their effect upon the animal system is counteracted in some degree by sugar. Liquid albumen forms insoluble compounds with these salts, and is an antidote to their poisonous action. Copper is separated in the metallic state from its salts by zinc, iron, lead, and the more oxidable metals, which are dissolved, and take the place of the former metal.

Potash, or *soda,* added to the solution of a cupric salt, throws down at first a blue precipitate of hydrated cupric oxide, which, however, on agitation, takes up a portion of the undecomposed salt, and forms with it a green basic salt. An excess of the alkali throws down the hydrated oxide in bulky blue flakes, which, on boiling the mixture, collect together in the form of a black powder, consisting of the anhydrous oxide. This reaction is greatly modified by the presence of fixed organic substances, such as sugar, tartaric acid, &c. In a solution of sulphate of copper, containing such substances in sufficient quantity, potash either produces no precipitate, or one which is quickly re-dissolved, forming a blue solution; and from this solution, when boiled, the copper is sometimes wholly precipitated as red or yellow cuprous oxide, as when grape-sugar is present, — or partially, as with cane-sugar, or not at all, as with tartaric acid. *Ammonia,* added by degrees, and with constant agitation, to the solution of a cupric salt, first throws down a green basic salt, and afterwards the blue hydrate: an excess of ammonia dissolves the precipitate, forming a deep blue solution. A copper solution, diluted so far as to be colourless, becomes distinctly blue on the addition of ammonia. The blue colour thus produced is still visible, according to Lassaigne, in a solution containing 1 part of copper in 100,000 parts of liquid. *Carbonate of potash* or *soda* throws down, with evolution of carbonic acid, a greenish blue precipitate of a basic carbonate of copper, which on boiling is converted into the black oxide. *Carbonate of ammonia* produces the same precipitate, but when added in excess, dissolves it abundantly, forming a blue solution. *Hydrosulphuric acid* and solutions of *alkaline sulphides* throw down a brownish black precipitate of protosulphide of copper, insoluble in sulphide of potassium or sodium, slightly soluble in sulphide of ammonium. *Ferrocyanide of potassium* forms with cupric salts a deep chocolate-coloured precipitate of ferrocyanide of copper. To very dilute solutions it imparts a reddish colour, which is even more delicate in its indications than the ammonia reaction, being still visible in a solution containing 1 part of copper in 400,000 parts of liquid, according to Lassaigne, and in 1,000,000 parts, according to Sarzeau. Ferrocyanide of copper dissolves in aqueous ammonia, and reappears when the ammonia is evaporated. This reaction serves to detect extremely small quantities of copper, even when associated with other metals. Thus, if a solution containing copper and iron be treated with excess of ammonia, a few drops of ferrocyanide of potassium added, the liquid filtered, and the filtrate left to evaporate in a small white porcelain capsule, ferrocyanide of copper will be left behind, exhibiting its characteristic red colour (Warington). Salts of copper impart a green colour to flame. The black oxide of copper dissolves by fusion in a vitreous flux, and produces a green glass. Any compound of copper fused with borax in the oxidizing flame of the blowpipe forms a transparent glass, which is green while hot, but assumes a beautiful blue colour when cold. In the reducing flame, the glass becomes opaque, and covered on the surface with liver-coloured streaks of cuprous oxide, or metallic copper. This last reaction is somewhat difficult to obtain, especially when the quantity of copper is small, but it may always be ensured by fusing a small piece of metallic tin in the bead. Copper salts mixed with carbonate of soda or cyanide of potassium, and heated on charcoal before the blowpipe, yield metallic copper.

Thénard obtained a higher oxide of copper, CuO_2, by the action of diluted bioxide of hydrogen on the hydrated protoxide of copper.

Chloride of copper, cupric chloride, CuCl, is obtained by dissolving the black oxide in hydrochloric acid. Its solution is green when concentrated, but blue when more dilute, and the salt forms blue prismatic crystals, containing two atoms of water. It combines with chloride of potassium, and more readily with chloride of ammonium, forming the double salts $KCl.CuCl + 2HO$, $NH_4Cl.CuCl + 2HO$. Another chloride of copper and ammonium, containing $NH_4Cl.2CuCl + 4HO$, is obtained in fine bluish-green crystals, by mixing the solution of 1 eq. sal-ammoniac and 2 eq. chloride of copper.

Chloride of copper likewise combines with ammonia, forming the three following compounds: — *a*. $3NH_3.CuCl$. This compound is obtained by saturating dry protochloride of copper with ammoniacal gas: it forms a blue powder. — *b*. $2NH_3.CuCl$. Formed by passing ammoniacal gas through a hot saturated solution of protochloride of copper, till the precipitate first formed is completely redissolved. During this process, the liquid is kept almost boiling by the heat developed by the absorption of the gas; and the resulting solution yields, on cooling, small dark blue octohedrons and square prisms with four-sided summits. — *c*. $NH_3.CuCl$. Obtained by heating *a* or *b* to 300°, or by saturating dry chloride of copper, at a high temperature, with ammoniacal gas. Forms a green powder. The compound *c* may also be regarded as *chloride of cuprammonium*, $NH_3Cu.Cl$, or *hydrochlorate of cupramine*, $NH_2Cu.HCl$, the base being ammonium or ammonia in which 1H is replaced by Cu. Similarly, *b* may be regarded as a *basic hydrochlorate of dicupramine*, $N_2H_5Cu.HCl$, the base being formed by the union of two atoms of ammonia into one, and the substitution therein of 1Cu for 1H. Lastly, *a* may be regarded as *basic hydrochlorate of tricupramine*, $N_3H_8Cu.HCl$; or again, *a* may be regarded as $NH\overbrace{Am_2Cu}.Cl$, and *b* as $NH_2\overbrace{Am\,Cu}.Cl$.

Carbonates of copper.—When a salt of copper is precipitated by an alkaline carbonate, a hydrated subcarbonate is produced containing 2 eq. of oxide of copper to 1 eq. carbonic acid. It is a pale blue bulky precipitate, which becomes denser and green when treated with boiling water. It is used as a pigment, and known as *mineral green*. The beautiful native green carbonate of copper, *malachite*, is of the same composition, $CuO.Co_2 + CuO.HO$. The finely crystallized *blue copper ore* is another subcarbonate. It may be represented as the neutral hydrated carbonate of copper, in combination with a similar carbonate of copper, in which the constitutional water is replaced by oxide of copper:

$$\left\{\begin{array}{l} CuO.CO_2+HO. \\ CuO.CO_2+CuO. \end{array}\right.$$

In the green carbonate, the constitutional water of the neutral carbonate of copper is replaced by hydrate of copper. The neutral carbonate of copper itself, of which the formula would be $CuO.CO_2+HO$, is unknown. According to Thomson,* the anhydrous subcarbonate $2CuO.CO_2$, occurs in the form of *mysorine*, which contains also ferric oxide and silica.

Sulphate of copper, Cupric sulphate, Blue vitriol, $CuO.SO_3.HO + 4HO$; 79·66 *or* 995·7 + 562·5.—This salt may be formed by dissolving copper in sulphuric acid diluted with half its bulk of water, with ebullition; the metal is then oxidated with formation of sulphurous acid. But the sulphate of copper is more generally prepared, on the large scale, by the roasting and oxidation of sulphide of copper; or by dissolving in sulphuric acid the oxide formed by exposing sheets of metallic copper to air at a red heat. It forms large rhomboïdal crystals of a sapphire-blue colour, containing 5 eq. of water, which lose their transparency in dry air: they are soluble in four times their weight of cold, and twice their weight of boiling water. Like the other soluble salts of copper, the sulphate has an acid reaction; it is used as an escharotic. The water in this salt may be reduced to 1 eq. at 212°; above 400° the salt is anhydrous and white. Although sulphate of copper does not crystallize alone with 7HO, yet, when mixed with the sulphates of magnesia, zinc, nickel, and iron, it crystallizes along with these isomorphous salts in the form of sulphate of iron. At a strong red heat it melts and loses acid.

The anhydrous sulphate absorbs $2\frac{1}{2}$ eq. of ammonia, and forms a light powder of a deep blue colour (H. Rose.) When ammonia is added to a solution of sulphate of copper, an insoluble subsulphate is first thrown down, which is redissolved as the addition of ammonia is continued, and the usual deep azure-blue ammoniacal solution formed. The ammoniacal sulphate may be obtained in beautiful indigo-blue crystals, by passing a stream of ammoniacal gas into a saturated hot solution of the sulphate: it is $CuO\,SO_3.HO+2NH_3$ (Berzelius). These crystals lose 1 eq. ammonia and 1 eq. water at 390° (Kane), and are converted into a green powder, $CuO.SO_3 + NH_3$, or $(NH_3CuO).SO_3$; by the cautious application of a heat not exceeding 500°, the whole of the ammonia may be got rid of, and sulphate of copper quite pure remains behind. Sulphate of copper forms the usual double salts with sulphate of potash and with sulphate of ammonia. A saturated hot solution of the double sulphate of copper and potash allows a remarkable double subsalt to precipitate in crystalline grains, $KO.SO_3 + 3(CuO.SO_3) + CuO.HO+3HO$. A corresponding seleniate is deposited, below the boiling point, and always in crystals. The ammoniacal and double salts of sulphate of copper may be represented thus:—

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* Outlines of Mineralogy.

Sulphate of copper (blue vitriol)...........	$CuO.SO_3,HO+4HO$
Sulphate of copper and potash.............	$CuO.SO_3,(KO.SO_3)+6HO$
Hydrated ammoniacal sulphate of copper,	$CuO.SO_3,HO+2NH$
Preceding salt dried at 300°...............	$(NH_3.CuO).SO_3$
Rose's ammoniacal sulphate	$CuO.SO_3+(NH_3CuO)SO_3+4NH_3$
Do. heated to 350°.........................	$CuO.SO_3+(NH_3CuO)SO_3$

The hydrated ammoniacal sulphate may also be regarded as $N\widehat{H_2(NH_4)Cu}.SO_4$ and Rose's ammoniacal sulphate as

$$\left.\begin{array}{l} N\widehat{H_2(NH_4)Cu} \\ N\widehat{H(NH_4)_2Cu} \end{array}\right\} 2SO_4.$$

Several *subsulphates of copper* have been formed. By digesting hydrated oxide of copper in a solution of sulphate of copper, a green powder is obtained, of which the constituents are, according to Berzelius, $3CuO.SO_3+3HO$. The bluish-green precipitate which falls when ammonia is added to sulphate of copper, or potash added in moderate quantity to the same salt, contains, according to Kane's and Graham's analyses, $4CuO.SO_3+4HO$. By a larger quantity of potash, Kane precipitated a clear grass-green subsulphate, containing $8CuO.SO_3+12HO$. The last subsulphate loses exactly half its water at 300°.*

Nitrate of copper, $CuO.NO_5 + 3HO$, is formed by dissolving copper in nitric acid. It crystallizes from a strong solution in blue prisms which contain 3 atoms of water, or in rhomboïdal plates which contain 6 atoms of water. This salt acts upon granulated tin, with nearly as much energy as hydrated nitric acid. A crystallized *ammoniacal nitrate of copper* is obtained by conducting a stream of ammoniacal gas into a saturated solution of nitrate of copper. It is anhydrous, and contains $NO_5.CuO + 2NH_3$ (Kane). It may be regarded as $N\widehat{H_2(NH_4)Cu}.NO_6$.

Subnitrate of copper, $CuO.NO_5 + 3(CuO . HO)$, according to the analyses of Gerhardt, Gladstone,† and Kuhn,‡ is a green powder, produced by the action of heat upon the neutral nitrate, at any temperature between 160° and 600°; or by adding to that salt a quantity of alkali insufficient for complete precipitation. When oxide of copper is drenched with the most concentrated nitric acid ($HO.NO_5$), it is this subsalt, singular as it may appear, which is formed, even when the acid is in great excess.

Oxalate of copper and potash is obtained by dissolving oxide of copper in binoxalate of potash; it crystallizes with 2 and with 4 eq. of water.

Acetates of copper.—The *neutral acetate*, $CuO.(C_4H_3O_3) + HO$, or $C^4H^3CuO^4 + HO$, is obtained by dissolving oxide of copper in acetic acid. It forms fine crystals of a deep green colour, containing 1 eq. of water, which lose their transparency in air, and are soluble in 5 times their weight of boiling water. This salt, when it separates from an acid solution below 40°, also forms blue crystals containing 5HO (Wöhler). The green salt is found in commerce under the improper name of *distilled verdigris*. The acetates of copper and potash unite in single equivalents, and form a double salt in fine blue crystals, containing 8HO. *Verdigris* is a subacetate of copper, formed by placing plates of the metal in contact with the fermenting marc of the grape, or with cloth dipped in vinegar. The bluer species, which consists of minute crystalline plates, is a definite comcompound of 1 eq. acetic acid, 2 eq. oxide of copper, and 6 eq. of water, $C_4H_3CuO_4.CuO + 6HO$. The ordinary green species is a mixture of the sesqui- and tribasic acetates of copper, with the preceding bibasic acetate. Water dissolves out from verdigris the *sesquibasic acetate*, which presents itself on evapo-

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* Transactions of the Royal Irish Academy, vol. xix. p. 1; or Ann. Ch. Phys. t. lxxii. p. 272.

† Chem. Soc. Mem. iii. 480.

‡ Arch. Pharm. [2.], l. 283.

rating the solution, sometimes as an amorphous mass, and sometimes in crystalline grains of a pale blue colour. The sesquibasic acetate consists of 2 eq. of acetic acid, 3 eq. of oxide of copper, and 6 eq. of water; it loses 3 eq. of water at 212°. The *tribasic acetate* is the insoluble residue which remains after the lixiviation of verdigris. It is a clear green powder, which loses nothing at 212°. It contains 2 eq. of acetic acid, 6 eq. oxide of copper, and 3 eq. of water (Berzelius).

Acetate of copper also combines with acetate of lime, and with several other salts. The double *acetate and arsenite of copper* is a crystalline powder of a brilliant sea-green colour, which is used as a pigment, under the name of Schweinfurt green. It is obtained by mixing boiling solutions of equal parts of arsenious acid and neutral acetate of copper, adding to the mixture its own volume of cold water, and leaving the whole at rest for several days. It is a highly poisonous substance. From the analysis of Ehrmann, its formula is $C_4H_3CuO_4 + 3(CuO.AsO_3)$.

The most important *alloys of copper* are those which it forms with tin and zinc:

100 parts of copper with 5 tin (or 4 tin + 1 zinc) form the bronze used for coin.
100 parts copper with 10 tin, form bronze and gun-metal.
100 parts copper with 20 to 25 tin, form bell-metal.
100 parts copper with 30 to 35 tin, form speculum-metal.

A little arsenic is generally added to the last alloy, to increase its whiteness.

The different varieties of brass are prepared, either by fusing together the two metals, copper and zinc, or by heating copper under a mixture of charcoal and calamine — an operation in which zinc is reduced and its vapour absorbed by the copper. Two or three parts of copper to one of zinc form common brass. The brass known as Muntz's white metal, which resists the solvent action of sea-water much better than pure copper, and is, in consequence largely used for the sheathing of ships, consists of 60 parts copper to 40 parts zinc, and appears to be the atomic compound Cu_2Zn. Equal parts of copper and zinc, or four of the former and one of the latter, give an alloy of a higher colour, resembling gold, and on that account called *similor*.

ESTIMATION OF COPPER, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Copper is best precipitated by caustic potash, which when added to a boiling solution of a cupric salt, throws down the protoxide of copper in the form of a heavy black powder. From this precipitate every trace of potash may be removed by washing with hot water; and the washed precipitate may then be dried and ignited in a platinum or porcelain crucible. It must be weighed immediately after cooling, with the cover on the crucible, because it absorbs moisture rapidly from the air. It contains 79·82 per cent. of copper (H. Rose).

Copper is often precipitated from its solutions by hydrosulphuric acid. In that case the precipitated sulphide must be washed as quickly as possible with water containing hydrosulphuric acid, to prevent oxidation; the precipitate may then be dried, and the filter burnt with the precipitate on it, in a porcelain basin; after which the precipitate is treated with concentrated nitric acid, which dissolves it, with separation of sulphur, and the copper precipitated from the filtered solution by potash as above. The chief precaution to be attended to in this process is to wash the precipitated sulphide quickly, and to preserve it as completely as possible from contact with the air; otherwise the sulphide becomes partially oxidized and converted into sulphate, which being soluble, runs through the filter; when this takes place, the filtrate becomes brown, because the copper thus carried through, is again precipitated by hydrosulphuric acid

Volumetric methods.—Copper may be volumetrically determined by means of a solution of permanganate of potash, by a process founded on that adopted by Margueritte for the determination of iron (p. 458). The copper compound having been weighed and dissolved in acid, is mixed in a porcelain basin, with neutral tartrate of potash and excess of caustic potash, and then heated with a quantity of milk-sugar, or honey, sufficient to precipitate all the copper as cuprous oxide, the completion of the precipitation being indicated by the brown colour which the liquid then acquires. The precipitated cuprous oxide is then filtered, washed with hot water, and gently heated, together with the filter, with a mixture of pure sesquichloride of iron and dilute hydrochloric acid. It is thereby dissolved in the form of protochloride of copper, the sesquichloride of iron being at the same time reduced to protochloride:

$$Cu_2O + Fe_2Cl_3 + HCl = 2CuCl + 2FeCl + HO.$$

In the filtered liquid, diluted to a convenient strength and heated to about 86°, the quantity of iron in the state of protochloride is determined by a graduated solution of permanganate of potash in the manner already described (p. 458), and thence the equivalent quantity of copper is readily determined. The presence of lead, zinc, bismuth, manganese, or iron, in the alkaline solution, does not interfere with the process; silver or mercury must be separated before the precipitation of the cuprous oxide.

Another method, which appears to give very exact results, is to treat the copper-solution with iodide of potassium, whereby diniodide of copper is precipitated and iodine set free:

$$2(CuO.NO_5) + 2KI = Cu_2 + I + 2(KO.NO_5),$$

and remove the free iodine by means of a standard solution of hyposulphite of soda, whereby iodide of sodium and tetrathionate of soda are produced:

$$2(NaO.S_2O_2) + I = NaI + NaO.S_4O_5.$$

The copper-compound, if solid, an alloy for example, is dissolved in nitric acid; carbonate of soda added till a slight precipitate is formed; and this precipitate redissolved in acetic acid (free nitric acid would vitiate the result by decomposing the iodide of potassium). A quantity of iodide of potassium is next added, equal to at least six times the weight of the copper to be determined, and then the standard solution of hyposulphite of soda, in sufficient quantity to remove the greater part of the free iodine, which point will be indicated by the colour of the liquid changing from brown to yellow. Lastly, a clear solution of starch is added, and the addition of the hyposulphite of soda cautiously continued till the blue colour of the iodide of starch is completely destroyed. The solution of hyposulphite of soda is graduated by dissolving a known weight of pure electrotype copper in nitric acid, and proceeding as above. If the copper-compound contains a large quantity of lead or iron, these metals must be removed before commencing the determination, because the yellow colour of the iodide of lead and the red of the acetate of iron might interfere with the result (E. O. Brown).*

Pelouze's method, which consists in treating the copper solution with excess of ammonia, and precipitating the copper as oxysulphide, $CuO.5CuS$, by adding a graduated solution of sulphide of sodium till the blue colour is completely destroyed, appears, from Mr. Brown's experiments, to be liable to uncertainty from two causes: first, because the oxysulphide of copper reduces a portion of the protoxide of copper to dioxide, thereby rendering the solution colourless before the precipitation is complete; and secondly, because a portion of the sulphide of sodium is oxidized and converted into hyposulphite of soda.

Copper is separated from all the preceding metals, except cadmium, by means

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* In a paper read before the Chemical Society, Nov. 17th, 1856, and to be published in the 10th volume of the Society's Journal.

of hydrosulphuric acid, the solution being previously acidulated with hydrochloric or sulphuric acid. When zinc, nickel, or cobalt is present, a considerable excess of acid must be added, otherwise a portion of these metals will be precipitated together with the copper.

From *cadmium*, copper may be separated by carbonate of ammonia, which dissolves the copper and leaves the cadmium. The deposition of the cadmium is not complete till the liquid has been exposed for some time to the air. The separation is, however, better effected by adding to the solution of the two metals a quantity of cyanide of potassium, sufficient to redissolve the precipitate first formed, and then passing hydrosulphuric acid through the solution. Sulphide of cadmium is then precipitated, and on driving off the excess of hydrosulphuric acid by heat, and adding more cyanide of potassium, the sulphide of copper remains completely dissolved. The copper may be precipitated as sulphide by mixing the filtrate with hydrochloric acid: but it is better to boil the filtrate with aqua-regia, till all the hydrocyanic acid is expelled, and then precipitate the copper by potash (Haidlen and Fresenius).

SECTION VIII.

LEAD.

Eq. 103·56 *or* 1294·5; Pb (*plumbum*).

Lead was one of the earliest known of the metals. A considerable number of its compounds are found in nature, but the sulphide, or galena, is the only one which is important as an ore of lead. The reduction of the metal is effected by heating the sulphide with exposure to air (or roasting), by which much of the sulphur is burned and escapes as sulphurous acid, and a fusible mixture of oxide of lead and sulphate of lead is produced. A fresh portion of the ore is added, which reacts upon the oxide of lead, the sulphur and oxygen forming sulphurous acid, and the lead of both oxide and sulphide being consequently reduced. Lime also is added, which decomposes the sulphate of lead, and exposes the oxide to be reduced by the fuel or by sulphide.

Lead has a bluish grey colour and strong metallic lustre, is very malleable, and so soft, when it has not been cooled rapidly, as to produce a metallic streak upon paper. Its density is 11·445, and is not increased by hammering. Its tenacity is less than that of any other ductile metal. The melting point of lead is 612°; on solidifying, this metal shrinks considerably, so that bullets cast in a mould are never quite round. Lead, like most other metals, assumes the octohedral form on crystallizing. Lead is one of the less oxidable metals, at least when massive; its surface soon tarnishes, and is covered with a grey pellicle, which appears to defend the metal from further change. Rain or soft water cannot be preserved with safety in leaden cisterns, owing to the rapid formation of a white hydrated oxide at the line where the metal is exposed to both air and water; the oxide formed is soluble in pure water, and highly poisonous. But a small quantity of carbonic acid, which spring and well water usually contain, arrests the corrosion of the lead, by converting the oxide of lead into an insoluble salt, and prevents the contamination of the water.* Lead is not directly attacked by hydrochloric and sulphuric acids, at the usual temperature, but they favour its union with oxygen from the air. Its best solvent is nitric acid. Besides a protoxide, PbO, which is a powerful base, lead forms a suboxide, Pb_2O, and a bioxide, PbO_2, which do not combine with acids.

Suboxide of lead, Pb_2O, was discovered by Dulong, and is best obtained by

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* Dr. Christison's Treatise on Poisons.

heating the oxalate of lead to low redness in a small retort. It is dark grey, almost black, and pulverulent, and is not affected by metallic mercury. According to the analysis of Boussingault, it contains 1 eq. of oxygen to 2 eq. of lead. The grey pellicle which forms upon lead exposed to the air is, according to Berzelius, the same suboxide.

Protoxide of lead, PbO, 111·56 *or* 1394 5.—When a stream of air is thrown upon the surface of melted lead, the metal is rapidly converted into the protoxide, of a sulphur-yellow colour. The oxidated skimmings of the metal are, in this condition, termed *massicot*, and were at one time used as a yellow pigment. This preparation is fused at a bright red heat, and the oxide is thus separated from some metallic lead, with which it is intermixed in massicot. The fused oxide, on solidifying, forms a brick-red mass, which divides easily into crystalline scales, tough and not easily pulverized; they form *litharge*. The protoxide of lead can be obtained distinctly crystallized by various processes, but always presents itself in the same form, an octohedron with a rhombic base (Mitscherlich). By igniting the subnitrate of lead, the protoxide is obtained very pure, and of a rich lemon-yellow colour. Its density after fusion is 9·4214.

When the acetate, or any other salt of lead, is precipitated by potash, the protoxide falls as a white hydrate, which may be dried at 212° without decomposition. It contains 3¾ per cent. water, and is, therefore, the hydrate $2PbO . HO$ (Mitscherlich). Oxide of lead likewise crystallizes anhydrous, from solution, at the usual temperature, when precipitated under such circumstances that it cannot find water to combine with. This oxide dissolves in above 12,000 times its weight of distilled water, which acquires thereby an alkaline reaction, but not in water containing any saline matter. It is soluble in potash or soda; and the solutions, when evaporated, yield small crystals of an alkaline compound. A compound of lime and oxide of lead is obtained in needles, when hydrate of lime and that oxide are heated together, and the solution allowed to evaporate with exclusion of air. This solution has been employed to dye the hair black. Oxide of lead combines readily with the earths and metallic oxides by fusion, and when added to the materials of glass, imparts brilliancy to it and increased fusibility.

Oxide of lead is a powerful base, resembling baryta and strontia, and affords a class of salts which often agree in form and in general properties with the salts of these earths. Its carbonate occurs in *plumbocalcite*, in the form of carbonate of lime, an isomorphism by which the protoxide of lead is connected with the magnesian oxides. All its soluble salts are poisonous, although no salt of lead, with the exception of the insoluble carbonate, is highly so (Dr. A. T. Thomson). In a case of accidental poisoning by the carbonate, acetic acid proved a sufficient antidote.

Caustic alkalies precipitate lead from its solutions as a white hydrate, soluble in potash and soda, insoluble in ammonia. *Alkaline carbonates* throw down a white precipitate of carbonate of lead, insoluble in excess of the reagent. *Hydrochloric acid* and *soluble chlorides* produce in moderately strong lead-solutions, a white crystalline precipitate of chloride of lead, easily soluble in potash, insoluble in ammonia, soluble in a considerable quantity of water; in dilute solutions (*e. g.* in a solution of 1 part of nitrate of lead in 100 parts of water) no precipitate is formed. *Sulphuric acid* and *soluble sulphates* throw down, even from very dilute solutions, a white, pulverulent precipitate of sulphate of lead, easily soluble in potash, soluble also, though slowly, in hydrochloric and nitric acid; but by adding a considerable excess of sulphuric acid, lead may be completely precipitated even from solutions containing hydrochloric or nitric acid. According to Lassaigne, 1 part of oxide of lead (in the form of nitrate) dissolved in 25,000 parts of water, gives an opalescence with sulphate of soda, after a quarter of an hour. *Hydrosulphuric acid* and *alkaline sulphides* produce a black precipitate of sulphide of lead, insoluble in sulphide of ammonium. In very dilute solutions, only a brown colouring is produced, the limit of the reaction being attained, according to Lassaigne, with 1 part of oxide of lead (in the form of nitrate) dissolved in 350,000 parts of water. If the solution of the lead-salt contains free hydrochloric acid, the precipitate is red or yellow, and a large excess of hydrochloric acid prevents it altogether. *Iodide of potassium* produces a bright yellow precipitate of iodide of lead, which dissolves in boiling water and separates again on cooling in crystalline spangles, exhibiting a beautiful play of colours. *Chromate* and *bichromate of potash* throw down yellow chromate of lead, easily soluble in caustic potash. The limit of this reaction is attained with 1 part of oxide of lead (in the form of nitrate) dissolved in 70,000 parts of water (Harting). *Iron* and *zinc* throw down metallic lead. If a mass of zinc be suspended in a solution, made by dissolving one ounce of acetate of lead in two pounds of distilled water, the lead is precipitated in beautiful crystalline plates, which are deposited not only in metallic contact with the zinc, but extend from it to a considerable distance in the liquid, forming what is called the lead-tree. Lead-salts, mixed with carbonate of soda or cyanide of potassium, and ignited on charcoal before the blow-pipe, yield a malleable button of lead. The oxides of lead are reduced by simply heating them with the blow-pipe flame on charcoal.

Sesquioxide of lead, Pb_2O_3. — Hypochlorite of soda throws down from lead-salts a reddish-yellow mixture of sesquioxide and chloride of lead. The sesquioxide may be obtained free from chloride by supersaturating a solution of nitrate of lead with potash, in quantity sufficient to redissolve the precipitated hydrate, and then treating it with hypochlorite of soda. The sesquioxide is converted by acids into bioxide and an ordinary salt of lead (Winkelblech).

Bioxide or peroxide of lead, PbO_2, may be obtained in the same manner as the peroxides of cobalt and nickel, by exposing the protoxide suspended in water to a stream of chlorine; also by fusing protoxide of lead with chlorate of potash at a temperature short of redness; or by digesting the following intermediate oxide, minium, in diluted nitric acid, which dissolves the protoxide of lead, decanting off the nitrate of lead, and washing the powder which remains with boiling water. Wöhler precipitates a solution of 4 parts of acetate of lead with a solution of 3 parts or rather more of crystallized carbonate of soda, and passes chlorine gas through the resulting thin pulpy mass, till the whole of the carbonate of lead is converted into brown bioxide, amounting to 2½ parts, which may then be washed. No chloride of lead is formed in this reaction, the whole of the chlorine combining with the sodium, while acetic and carbonic acid are set free. Bioxide of lead is of a dark earthy-brown colour. It loses half its oxygen by ignition; absorbs sulphurous acid with great avidity, and becomes sulphate of lead; and affords chlorine when digested in hydrochloric acid.

Minium or red lead is formed by heating massicot or protoxide of lead, which has not been fused, to incipient redness in a flat furnace, of a particular construction, and directing a current of air upon its surface. Oxygen is absorbed, and an oxide formed of a fine red colour, with a shade of yellow. It is not constant in composition. The proportion of oxygen, when the absorption is least considerable, approaches that of a compound containing $3PbO.PbO^2$; and such was the composition of a crystallized compound of a fine red colour, formed by accident in a minium furnace, and analyzed by Houton-Labillardière. But when the absorption is favoured by time and most considerable, it approaches but never exceeds 2·4 per cent. of the original weight of the protoxide. This result agrees with the formula Pb_3O_4, and accordingly minium may be regarded as a compound of protoxide and bioxide of lead, $2PbO.PbO_2$, or of protoxide and sesquioxide, $PbO.Pb_2O_3$. A sample of minium analyzed by Longchamps contained $5PbO.PbO_2$. The finest minium is obtained by calcining oxide of lead from the carbonate, at about 600°.

Minium is not altered by being heated in a solution of acetate of lead, which is capable of dissolving free protoxide of lead. When heated to redness, it loses oxygen, and leaves the protoxide. It does not combine with acids, but is resolved by a strong acid into bioxide of lead and protoxide, the latter combining with the acid. When minium is treated with concentrated acetic acid, it first becomes white, and then dissolves entirely in a new quantity of acid without colouring it. But the solution gradually decomposes, and bioxide of lead separates from it of a blackish-brown colour (Berzelius).

Protosulphide of lead, PbS, is thrown down from salts of lead, by hydrosulphuric acid, as a black precipitate, which is insoluble in diluted acids or in alkalies. It forms also the ore galena, which crystallizes in the cube and other forms of the regular system; its density is 7·585. Sulphide of lead is decomposed easily by nitric acid, and converted into nitrate and sulphate of lead, with separation of a little sulphur. The more concentrated the nitric acid, the greater is the quantity of sulphate produced. Recently precipitated sulphide of lead may be completely dissolved in the form of nitrate by boiling with dilute nitric acid. Concentrated and boiling hydrochloric acid dissolves sulphide of lead, with disengagement of hydrosulphuric acid gas. Galena may be united by fusion with more lead, and gives the subsulphides Pb_4S, and Pb_2S. When a solution of persulphide of potassium is added to a salt of lead, a blood-red precipitate appears, which is a persulphide of lead, but is almost immediately changed into the black protosulphide of lead and free sulphur.

Chloride of lead, PbCl, 139·06 *or* 1738·25. — Lead dissolves slowly in hydrochloric acid, by substitution for hydrogen, forming the chloride of lead, but only when assisted by the action of the air. The same compound is obtained by digesting oxide of lead in hydrochloric acid, and also falls as a white precipitate, when a salt of lead is added to any soluble chloride. The chloride of lead is soluble in 135 times its weight of cold water, and more so in hot water, from which it crystallizes on cooling in long flattened acicular crystals, which are anhydrous. It is very fusible, and may be sublimed at a higher temperature.

Oxychloride of lead. — Chloride of lead combines in five different proportions with the protoxide, forming the following compounds: — *a.* 3PbCl.PbO. Four parts of chloride of lead ignited with 1 part of litharge yield a fused, laminar, pearl-grey mixture, which, when triturated with water, swells up to a bulky mass having the above composition (Vauquelin). The same substance is obtained by Mr. Pattinson, by decomposing carbonate of lead with lime-water, and used as a white pigment. — *b.* PbCl.PbO. Formed by igniting chloride of lead in contact with air till it no longer fumes, or by fusing chloride and carbonate of lead together. Carbonic acid is then set free, and a compound formed which is of a deep yellow colour while fused, but as it cools assumes a lemon-yellow colour, and becomes nacreous and crystalline (Döbereiner).—*c.* PbCl 2PbO. This compound forms the mineral *Mendipite*, found at Mendip, in Somersetshire, where it occurs in yellowish-white, right rhombic prisms, which are harder than gypsum, translucent, and have an adamantine lustre (Berzelius). It also occurs, and in a state of greater purity, at Brilon, near Stadtbergen, in Westphalia; the crystals there found are white, translucent, and have a mother-of-pearl lustre on the cleavage surfaces.* — *d.* PbCl.3Pbo. Obtained by fusing 1 eq. chloride of lead with 3 eq. of the protoxide; also in the hydrated state, PbCl.3PbO + HO or 4PbO.HCl, by decomposing chloride of lead with ammonia; by precipitating subacetate of lead with common salt; and by decomposing a solution of common salt with protoxide of lead. The hydrate is a white flocculent mass, and when fused yields the anhydrous compound, which is a greenish-yellow laminated mass, forming a yellow powder. — *e.* PbCl.5PbO. Obtained by fusing 1 eq. chloride of lead with 5 eq. of the protoxide. Orange-yellow substance, yielding a deep yellow powder. — *f.* PbCl.7PbO, is produced on fusing by heat a mixture of 10 parts of pure oxide of lead and 1 part of pure sal-ammoniac, a portion of the lead being at the same time reduced. The surbasic chloride when fused affords cubic crystals on cooling slowly. It forms in that state a beautiful yellow pigment, known as Turner's

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* **Rhodius, Ann. Ch. Pharm. lxii. 373.**

yellow in this country, and Cassel yellow in Germany. It was prepared in England by digesting litharge with half its weight of common salt, a portion of which is converted into caustic soda, and afterwards washing and fusing the oxychloride formed. But it is sufficient to use 1 part of salt to 7 parts of oxide of lead in this decomposition.

Bichloride of lead, $PbCl_2$. — Bioxide of lead dissolves, without evolution of gas, in cold dilute hydrochloric acid, forming a rose-coloured liquid, from which alkalies throw down the bioxide in its original state. The rose-coloured acid solution, evaporated in vacuo over strong potash-ley, yields crystals of chloride of lead, PbCl, together with crystals of a different character, which appear to consist of $PbCl_2$, (Rivot, Beudant, and Daguin).

Bromide of lead, PbBr, is much less soluble in water than the chloride; hence, in a liquid containing hydrochloric and hydrobromic acids, if the bromine be precipitated by acetate of lead, the filtered liquid will still contain chlorine, which may then be detected by adding nitrate of silver (H. Rose).

Iodide of lead, PbI, 229·92 *or* 2874. — Appears as a beautiful lemon-yellow powder, when iodide of potassium is added to a salt of lead. It is soluble in 194 parts of boiling water, and in 1235 parts of water at the usual temperature, and may be obtained from solution in brilliant hexagonal scales of a golden-yellow colour. A compound of a paler yellow, which appears in dilute solutions and when the salt of lead is in excess, is a basic iodide. M. Denot finds three oxy-iodides of lead, containing 1 eq. of iodide of lead to 1 eq., 2 eq., and 5 eq., of oxide of lead, and always 1 eq. of water, which last they do not lose below a temperature of about 400°.

Neutral iodide of lead, PbI, is decomposed by metallic chlorides, yielding, when the iodide is in excess, compounds which may be regarded as iodide of lead, in which part of the iodine is replaced by chlorine. Sesquichloride of iron and protochloride of copper separate free iodine (A. Engelhardt).

Cyanide of lead, PbCy, is a white insoluble powder, obtained by precipitation.

Carbonate of lead, ceruse, white lead; $PbO.CO_2$; 133·56 *or* 1669·5.—Occurs in nature well crystallized, in the form of carbonate of baryta. It is precipitated as a white powder, of which the grains, although very minute, are crystalline, when an alkaline carbonate is added to the acetate or nitrate of lead. The precipitate is anhydrous. When oxide of lead is left covered with water in an open vessel, it absorbs carbonic acid, and becomes white, forming the subcarbonate, $PbO.CO_2 + PbO\,HO$.

Carbonate of lead is invaluable as a white pigment, from its great opacity, which gives it that property called *body* by painters, and enables it to cover well. As precipitated by an alkaline carbonate, it is deficient in body, owing to the transparency of the crystalline grains composing the precipitate. It is also a neutral carbonate, as thus prepared, and differs in composition from the ceruse of commerce, which Mulder finds always to contain hydrated oxide of lead in combination with the carbonate of lead. The result of Mulder's analyses of numerous specimens of white lead, is, that there are three varieties of that substance, the composition of which is expressed by the three following formulæ: —

$$2(PbO.CO_2) + PbO.HO;$$
$$5(PbO.CO_2) + 3(PbO.HO);\ \text{and}$$
$$3(PbO.CO_2) + PbO.HO.$$

Mr. J. A. Phillips has also examined several specimens of white lead prepared by the Dutch process. Four samples gave by analysis the formula, $2(PbO.CO_2) + PbO.HO$; one gave $3(PbO.CO_2) + PbO.HO$; another, $5(PbO.CO_2) + PbO.HO$.* Dr. T. Richardson also found that varieties of white lead contain a portion of oxide of lead, in addition to the carbonate, and so far confirms the conclusions of Mulder.

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* Chem. Soc. Qu. Pt. iv. p. 165.

In the old or Dutch mode of preparing white lead, which is still extensively practised, thin sheets of the metal are placed over gallipots containing weak acetic acid (water with about 2½ per cent. dry acid), themselves imbedded in fermenting tan, the temperature of which varies from 140° to 150°. The action is often very rapid, and the metal disappears in a few weeks to the centre of the sheet. In this process, from 2 to 2½ tons of lead (4480 to 5600 pounds) are converted into carbonate, by a quantity of vinegar which does not contain more than the small quantity of 50 pounds of dry acetic acid. Hence the metal is certainly neither oxidized nor carbonated in this process, at the expense of the acetic acid. The oxygen must be derived from the air, and the carbonic acid from the fermenting tan. In the newer process, litharge, without any preparation, is mixed with water and about 1 per cent. of acetate of lead, and carbonic acid gas passed over it; the oxide of lead is rapidly converted into excellent ceruse. There can be little doubt that all the oxide of lead is successively dissolved by the acetate, and presented to the carbonic acid as a soluble subacetate: a compound which, it is known, absorbs carbonic acid with the greatest avidity, and allows its excess of oxide to precipitate as carbonate of lead. The new process supplies likewise the theory of the old one, the function of the acetic acid being manifestly the same in both processes. Nitrate of lead has been substituted for the acetate, with other things the same as in the last process.

Sulphate of lead; PbO, SO_3; 151·56 *or* 1894·5. — This salt is precipitated when sulphuric acid or a soluble sulphate is added to a solution of acetate or nitrate of lead, as a white, dense, insoluble precipitate, which appears by the microscope to be composed of minute crystals. It is also formed by the action of strong nitric acid on sulphide of lead. Sulphate of lead contains in 100 parts, 26·44 sulphuric acid and 73·56 oxide of lead, and may be exposed to a red heat without decomposition. Dr. Richardson finds that this salt acquires considerable opacity, and may be substituted for ceruse, when prepared in a mode analogous to the new process for that substance; namely, by supplying sulphuric acid, in a gradual manner, to a thick mixture of litharge and water containing a small proportion of acetate of lead. In this manner the sulphate of lead may be obtained united with any desirable excess of oxide of lead.

Nitrate of lead; $PbO.NO_5$; 165·56 *or* 2069·5. — Obtained by dissolving litharge, at the boiling point, in slightly diluted nitric acid, which should be free from hydrochloric and sulphuric acids. The neutral nitrate crystallizes in large octohedrons, with the secondary faces of the cube, sometimes transparent, although generally white and opaque. The crystals are anhydrous; they are soluble in 7½ times their weight of cold, and in a much smaller quantity of hot, water. Nitrate of lead is decomposed by an incipient red heat, yielding a mixture of oxygen gas and peroxide of nitrogen (which is prepared in this way), and leaving the yellow oxide of lead. When a small quantity of ammonia is added to nitrate of lead, or when a dilute solution of the neutral salt is boiled with oxide of lead in fine powder, a soluble *bibasic nitrate of lead* is formed, $PbO.NO_5 + PbO$. It crystallizes during evaporation in fine scales, or in little opaque grains, which are anhydrous. The granular crystals decrepitate when heated, with extraordinary force. The *tribasic nitrate of lead* precipitates when ammonia is added in very slight excess to a solution of nitrate of lead. Its constituents are $2(3PbO.NO_5)+3HO$ (Berzelius). It is a white powder, which is soluble to a small extent in pure water. When nitrate of lead is digested with a considerable excess of ammonia, the decomposition stops at the point at which 6 eq. of oxide of lead are combined with 1 eq. of nitric acid. The *sexbasic nitrate of lead* contains $2(6PbO.NO_5 + 3HO$ (Berzelius).

Nitrites of lead. — When a solution of 100 parts of nitrate of lead is boiled with 78 parts of metallic lead in thin turnings, the lead is dissolved, and a little nitric oxide is evolved, in consequence of a partial decomposition of nitrous acid previously formed. The solution is alkaline and yellow; and gives, on cooling.

brilliant crystalline plates of a golden yellow colour, which consists of the *bibasic nitrite of lead*, $2PbO.NO_3$. By dissolving 100 parts of this salt in water at 167° (75°C.), and then mixing with the solution 35 parts of oil of vitriol, previously diluted with four times its weight of water, one half of the oxide of lead is precipitated as sulphate of lead, and a solution is obtained of a deep yellow colour, from which the *neutral nitrite of lead*, $PbO.NO_3+HO$, crystallizes. This salt gives yellow crystals, resembling the nitrate in form. Its solution absorbs oxygen from the air, and, like all the nitrites, gives off nitric oxide at 176 (80°C.), while a subnitrite of lead precipitates. Berzelius, to whom we are indebted for the preceding facts, also formed a *quadribasic nitrite of lead*, containing $NO_3.4PbO+HO$, by boiling 1 part of nitrate of lead, and 1½ parts or more of metallic lead, in a long-necked flask for 12 hours, then filtering and leaving the solution to crystallize by cooling: it thus yields pale, flesh-coloured, silky needles, or, if rapidly coolod, a white powder.

The nitrites of lead have also been examined by other chemists, who have obtained results differing from those of Berzelius. Thus, Péligot and others found that Berzelius's bibasic nitrite contains the elements of 2 eq. of oxide of lead, 1 eq. of hyponitric acid, NO_4, and 1 eq. of water. Gerhardt therefore regards it as a compound of bibasic nitrate and bibasic nitrite of lead:—

$$2(PbO.NO_4) = 2PbO.NO_3 + 2PbO.NO_5.$$

and expresses its formation by the equation:—

$$2(PbO.NO_5) + 2Pb = 2PbO.NO_5 + 2PbO.NO_3.$$

If the action of the metallic lead be further continued, a fresh portion of nitrate is deoxidized, and the result is an orange-coloured salt, containing $7PbO.2NO_4$ (Péligot), which Gerhardt regards as a double salt more basic than the former:

$$7PbO.2NO_4 = 4PbO.NO_3 + 3PbO.NO_5.$$

Finally, by the continued action of the lead, the subnitrate contained in these two salts is likewise reduced, and a subnitrite is formed, viz., either Berzelius's quadrobasic salt, $4PbO.NO_3$, or a bibasic nitrite $2PbO.NO_3$, obtained by Bromeis. The last salt crystallizes in long golden-yellow needles containing 1 eq. of water.*

Phosphate of lead.—On mixing nitrate of lead with ordinary phosphate of soda, a precipitate is formed containing the two salts $3PbO.PO_5$ and $2PbO.HO.PO_5$. The latter is obtained pure by precipitating a boiling solution of nitrate of lead with pure phosphoric acid. This salt dissolves in nitric acid and fixed alkalies, but very sparingly in acetic acid; ammonia converts it into $3PbO.PO_5$. It fuses readily before the blow-pipe, and crystallizes on cooling in well defined polyhedrons. When strongly ignited with charcoal, it gives off phosphorus and carbonic oxide, and leaves metallic lead.

Chlorite of lead, $PbO.ClO_3$, is obtained in sulphur-yellow crystalline scales by precipitating nitrate of lead with an excess of chlorite of baryta containing free chlorous acid. It decomposes at 259° with a kind of explosion, and sets fire to flowers of sulphur triturated with it. Sulphuric acid diluted with an equal weight of water, decomposes it, especially between 104° and 122°, evolving pure chlorous acid gas, and leaving 88.75 per cent. of sulphate of lead (Millon).

Chlorate of lead, $PbO.ClO_5 + HO$, is obtained by cooling a hot solution of oxide of lead in aqueous chloric acid, in rhomboïdal prisms belonging to the oblique prismatic system, and isomorphous with the analogously constituted crystals of chlorate of baryta. These crystals, when heated, leave the yellow oxychloride, $PbO.2PbCl$ (Vauquelin, Wächter, Vogel).

Perchlorate of lead, $PbO.ClO_7$.—The solution of oxide of lead in warm aqueous

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* **For a more detailed account of the nitrates and nitrites of lead, see Gmelin's Handbook, Translation, v. 152—157.**

perchloric acid, yields small prisms having a sweet but highly astringent taste, soluble in their own weight of water, but not deliquescent (Serullas). By boiling a concentrated solution of this salt with carbonate of lead, a solution of a basic salt is obtained, which if the excess of base is very large, yields by evaporation, dull, indistinct crystals, which are resolved by water into a solution of bibasic salt, and a white insoluble residue. When the excess of base is less, or when the solution of the bibasic salt is left to evaporate, crystals of two different forms are obtained; both, however, containing $2PbO.ClO_7 + 2HO$ (Marignac).

Chlorophosphate of lead, $PbCl + 3(3PbO.PO_5$, occurs as *pyromorphite* and *green* and *brown lead-ore.* The crystals belong to the hexagonal system, and have the hardness of apatite. It fuses readily, and on cooling solidifies with vivid incandescence into an angular crystalline mass. In some of these ores, the chloride of lead is partly replaced by fluoride of calcium, and the triphosphate of lead by the triphosphate of calcium or trisarseniate of lead. The calcareous ores may be regarded as mixtures of apatite and pyromorphite. The same compound containing, however, an atom of water, is formed artificially on pouring a boiling solution of chloride of lead into a boiling solution of phosphate of soda, the latter being in excess (Heintz). When, on the contrary, a boiling solution of phosphate of soda is poured into an excess of chloride of lead, a precipitate is formed, which, according to Heintz, is $2(3PbO.PO_5) + PbCl$, but, according to Gerhardt, $2PbO.HO.PO_5 + PbCl$.

Acetate of lead, $PbO.(C_4H_3O_3) + 3HO$.—This salt is met with well crystallized, and in a state of great purity, in commerce. It is generally prepared by dissolving litharge in the acetic acid procured by the distillation of wood. It crystallizes in flattened four-sided prisms; has a taste which is first sweet and then astringent; is very soluble in water, 100 parts of water dissolving 59 of the salt at 60°; and dissolves in 8 parts of alcohol. It effloresces in air, and is apt to be partially decomposed by the carbonic acid of the air, and thus to become partially insoluble. It loses the whole of its water when dried at the usual temperature in vacuo. M. Payen crystallized the anhydrous acetate from solution in absolute alcohol.

Tribasic subacetate of lead, $PbO.(C_4H_3O_3) + 2PbO$, is formed by digesting oxide of lead in a solution of the neutral salt, till it is strongly alkaline. This salt does not crystallize when so prepared, but may be dried, and then contains no water. It is very soluble, but must be dissolved in distilled water, as the carbonic, hydrochloric and other acids in well water precipitate its oxide of lead. M. Payen has observed that the tribasic subacetate crystallizes readily, in fine prismatic needles, when formed by adding ammonia to a moderately strong solution of the neutral acetate. The crystals contain 1 eq. of water, which they lose at 212°. The acetate of ammonia, formed at the same time, appears to give stability to the subacetate of lead in solution, and prevents an excess of a whole equivalent of ammonia from throwing down any oxide of lead from the solution. This ammoniacal solution of the subacetate of lead, prepared without an excess of ammonia, is a convenient form in which to apply that salt as a reagent.*

Sesquibasic acetate of lead, $3PbO.2(C_4H_3O_3) + HO$. —This salt was obtained by Payen by adding 1 eq. of the neutral acetate to a concentrated and boiling solution of 1 eq. of the tribasic acetate. It is also produced when the neutral and anhydrous acetate of lead is heated in a retort or porcelain capsule, till the whole, after being liquid, becomes a white and porous mass. The sesquibasic acetate is then formed by the decomposition of 3 eq. of neutral acetate of lead, from which there separate the elements of 1 eq. of acetic acid, in the form of carbonic acid and acetone (Matteucci and Wöhler). This basic salt is very soluble, and crystallizes in plates of a pearly lustre. Another method of obtaining it is to digest an aqueous

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* Mémoires sur les Acétates et le Protoxide de Plomb, par M. Payen, An. de Chim. et de Phys. t. lxvi. p. 37.

solution of 2 eq. of the neutral acetate with 1 eq. of protoxide of lead free from carbonate, till it dissolves, and evaporate the filtrate in vacuo over oil of vitriol.

A *sexbasic acetate of lead*, $6PbO.(C_4H_3O_3)$, is formed on dropping a solution of the neutral, or of tribasic acetate of lead, into excess of ammonia. It is a white precipitate, which when examined by the microscope, has a crystalline aspect. It contains a little water, which it loses when dried in vacuo.

A *bibasic acetate of lead*, $2PbO.(C_4H_3O_3)$, is also formed, according to Döbereiner and Schindler, by boiling 1 eq. of neutral acetate of lead with 1 eq. of the protoxide.

The common *extractum Saturni* of the pharmacopœias appears to consist chiefly of bibasic acetate, containing more or less of the tribasic and sesquibasic salts.

Alloys of lead. — Lead and tin may be fused together in all proportions. M. Rudberg finds that these metals combine in certain definite proportions, having fixed points of congelation: —

1 atom of lead and 3 atoms of tin, congeal at 368.6°.
1 atom of lead and 1 atom of tin, at 464°.
2 atoms of lead and 1 atom of tin, at 518°.
3 atoms of lead and 1 atom of tin, at 536°.

A thermometer placed in a fluid alloy of 1 atom of lead and 2 atoms of tin, becomes stationary when the temperature falls to 392°; a portion then solidifies, and a more fusible alloy separates; the temperature again falls, and afterwards becomes stationary at 368·6°, the crystallizing point of the alloy composed of 1 atom of lead and 3 atom of tin. If the alloy contains so much tin that its point of complete congelation is below 368·6°, the last compound always separates from it at that point, and the thermometer remains stationary for a time, whatever may be the proportion of the metals in the alloy.* *Fine solder* is an alloy of 2 parts of tin and 1 of lead; it fuses at about 360°, and is much employed in tinning copper. *Coarse solder* contains one-fourth of tin, and fuses at about 500°; it is the substance employed for soldering by plumbers.

Lead, as reduced from the native sulphide, always contains a little silver. The latter is separated by allowing two or three tons of the melted metal to cool slowly in a hemispherical iron pot, when the lead, as it solidifies, separates in crystals, which can be raked out. The silver remains almost wholly in the more fusible portion, or what may be looked upon as the mother-liquor of these crystals; so that by this operation the argentiferous alloy is greatly concentrated. This mode of separation was discovered by Mr. Pattinson of Newcastle. To separate the remaining lead, much of it is converted into massicot, by the action of air upon its surface, in the shallow furnace used for that preparation; and the last portions of lead are removed by continuing the oxidation upon a porous bason or *cupel* of bone-earth, which imbibes the fused oxide of lead, while the melted silver is found in a state of purity upon the surface of the cupel, not being oxidable at a high temperature.

ESTIMATION OF LEAD, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Lead may be estimated either as protoxide or as sulphate. For the former mode of estimation, it is best to precipitate by oxalate of ammonia, the solution being neutral or rendered very slightly alkaline by ammonia. The oxalate of lead, after being washed and dried, is then to be ignited in an open procelain crucible, whereby it is converted into protoxide. As lead is very easily reduced by carbonaceous matter at a red heat, the precipitate must not be ignited in contact with the filter; but the filter, after the greater part of the precipitate has been removed from it, must be held on the point of a fine platinum wire above the crucible, and set on fire, so that the ashes may drop in; the precipitate may then be added, and

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* Rudberg, An. Ch. Phys. [2], xlviii. 363.

the ignition completed. The protoxide contains 92·83 per cent. of metallic lead. Lead may also be precipitated by carbonate of ammonia, to which a little free ammonia has been added, and the carbonate of lead treated as above.

In precipitating lead as sulphate, if the solution be neutral, the precipitation is best effected by sulphate of soda; the sulphate of lead may then be washed on a filter, dried and ignited; but if the solution contains free nitric acid, it is best to precipitate by excess of sulphuric acid, then evaporate to dryness, and ignite till all excess of acid is driven off; treat the residue with water to dissolve out any soluble salts that may be present; wash the sulphate of lead on a filter, and then dry and ignite it, burning the filter separately as above. The sulphate contains 68·32 per cent. of lead.

From the *alkalies* and *earths*, and from *manganese*, *iron*, *cobalt*, *nickel* and *zinc*, lead is easily separated by hydrosulphuric acid, the solution being previously acidulated with nitric acid. The precipitated sulphide is washed and dried, then placed, together with the filter (which should be as small as possible), in a porcelain dish, covered over with a glass plate or a funnel, and treated with fuming nitric acid, added cautiously and by small portions at a time. Violent action takes place, and the sulphide of lead is converted into sulphate. A portion may, however, be converted into nitrate, with separation of sulphur: hence, to insure complete conversion into sulphate, it is necessary to add a few drops of strong sulphuric acid. The product must then be strongly ignited to drive off the excess of sulphuric acid, and burn away the remaining organic matter of the filter.

From *cadmium* and *copper*, lead is easily separated by sulphuric acid.

ORDER V.

OTHER METALS PROPER HAVING ISOMORPHOUS RELATIONS WITH THE MAGNESIAN FAMILY.

SECTION I.

TIN.

Eq. 58·82 *or* 735·25; Sn (*stannum*).

TIN does not occur native, but its common ore is reduced by a simple process, and mankind appear to have been in possession of this metal from the earliest ages. The most productive mines of tin are those of Cornwall, from which the ancients appear to have derived their principal supply of this metal, and those of the peninsula of Malacca, and island of Banca, in India.

The only important ore of tin is the bioxide, which is found in Cornwall, both in veins traversing the primary rocks, and in alluvial deposits in their neighbourhood. In the latter case, the ore presents itself in rounded grains of greater or less size, which form together a bed covered by clay and gravel. This ore has evidently been removed from its original situation, and the grains rounded by the action of water, which has at the same time divested it of the other metallic ores with which it is accompanied in the vein; these being softer are more easily reduced to powder, and have been carried away by the stream. This ore, called *stream tin*, is easily reduced by coal, and gives the purest tin. The metal from the ore of the veins is contaminated with iron, copper, arsenic, and antimony, from which a portion of it is partially purified by *liquation*. Bars of the impure metal are exposed to a moderate heat, by which the pure tin is first melted, and separates it from a less fusible alloy containing the foreign metals. The purer portion is called *grain tin*, and the other, *ordinary tin* or *block tin*. The mass of grain tin is heated till it becomes brittle, and then let fall from a height. By this it splits into irregular prisms, somewhat resembling basaltic columns. This splitting is a mark of the purity of the tin, for it does not happen when the tin is contaminated by other metals.

Pure tin is white, with a bluish tinge, very soft, and so malleable, that it may be beaten into thin leaves, tinfoil not being more than 1-1000th of an inch in thickness. When a bar of tin is bent, it emits a grating sound, which is characteristic; and when bent backwards and forwards rapidly, several times in succession, becomes so hot that it cannot be held in the hand. At the temperature of boiling water, tin can be drawn out into wire, which is very soft and flexible, but deficient in tenacity. The density of pure tin is 7·285, or 7·293 after being laminated; that of the tin of commerce is said to vary from 7·56 to 7·6. Its point of fusion is 442°, according to Crichton and Rudberg; 4456°, according to Kupffer. Tin is volatile at a very high temperature. The brilliancy of the surface of tin is but slowly impaired by exposure to air, and even in water it is scarcely acted upon. Hence the great value of this metal for culinary vessels, and for covering the more oxidable metals, such as iron and copper, when employed as such. Three oxides of tin are known, the protoxide, SnO, sesquioxide, Sn_2O_3, and binoxide, SnO_2.

Protoxide of tin, Stannous oxide; SnO, 66·82 *or* 835·25. Tin dissolves in undiluted hydrochloric acid, at the boiling temperature, by substitution for hydrogen, and forms the protochloride of tin. From this the protoxide is precipitated by an alkaline carbonate, as a white hydrate, which may be washed with tepid water and dried at a temperature not exceeding 176°. It does not contain a trace of carbonic acid. This white powder dried more strongly in a retort filled with carbonic acid, and heated to redness, gives the anhydrous oxide as a black powder, the density of which is 6·666. In this state, the oxide is permanent; but if a body at a red heat is brought in contact with it in open air, it takes fire and burns, and is entirely converted into bioxide. If hydrated stannous oxide be boiled with a quantity of potash not sufficient to dissolve it entirely, the undissolved portion is converted into small, hard, shining, black crystals of anhydrous stannous oxide, which, when heated to 392°, decrepitate, swell up, fall to pieces, and are converted into an olive-green powder, consisting also of the anhydrous protoxide. Again, on evaporating a very dilute solution of sal-ammoniac, in which hydrated stannous oxide is diffused, that compound is converted, as soon as the sal-ammoniac crystallizes, into anhydrous stannous oxide, having the form of a cinnabar-coloured powder. There are, therefore, three modifications of stannous oxide, black, olive-green, and red (Fremy). The red modification is also obtained by digesting thoroughly washed hydrated stannous oxide at a temperature of 133°, in a slightly acid solution of stannous acetate, having a density of 1·06 (Roth).

Protoxide of tin dissolves in acids, and with more facility when hydrated than after being ignited. This oxide is also dissolved by potash and soda, but the solution after a time undergoes decomposition; metallic tin is deposited, and the bioxide is found in solution. The solution of a stannous salt, and of a stannic salt also, is apt to undergo decomposition, when largely diluted with water, and to deposit a subsalt. Stannous salts absorb oxygen from the air, and have a great affinity for that element; they convert the sesquioxide of iron into protoxide, and throw down mercury, silver and platinum in the metallic state from their solutions. *Chloride of gold* produces a purple precipitate in a stannous salt, consisting, it is believed, of the bioxide of tin in combination with protoxide of gold, a test by which the protoxide of tin may always be distinguished. *Hydrosulphuric acid* produces in neutral or acid solutions of stannous salts, a brown-black precipitate of protosulphide of tin, which, when gently heated with a considerable quantity of sulphide of ammonium containing excess of sulphur, is converted into the bisulphide and dissolved; acids added in excess to this solution precipitate the yellow bisulphide. *Caustic alkalies* and *alkaline carbonates*, added to stannous salts, throw down a white precipitate of hydrated stannous oxide, soluble in caustic potash or soda, but not in ammonia. *Ferrocyanide of potassium* produces a white precipitate, soluble in hydrochloric acid.

Protosulphide of tin, SnS, is formed when sulphur is mixed with tin heated above its melting point; it is also obtained in small dark grey crystalline laminæ, of sp. gr. 4·973, by adding the hydrated sulphide precipitated from a stannous salt by hydrosulphuric acid, to anhydrous protochloride of tin in the melted state, and removing the excess of the protochloride with dilute hydrochloric acid. It is decomposed by dilute hydrochloric acid, with evolution of hydrosulphuric acid.

Protochloride of tin, *Salt of tin;* SnCl. — This salt may be obtained in the anhydrous state by gradually heating a mixture of equal weights of calomel and tin, and finally distilling the protochloride at a strong red heat. The fused mass on cooling forms a grey solid, of considerable lustre, and having a vitreous fracture. The hydrated chloride, known in commerce as salt of tin, is procured by evaporating the solution of tin in concentrated hydrochloric acid to the point of crystallization. It is thus obtained in needles, or in larger four-sided prismatic crystals containing 2 eq. of water. They fuse between 100° and 105°. The specific gravity of the crystals is 2·710 at 60°; that of the fused mass at 100°, is 2·588 (Penny). The salt parts with the greater portion, if not the whole of its water at 212°, but if distilled at a higher temperature, loses hydrochloric acid also, and leaves an oxychloride of tin. It dissolves completely in a small quantity of water; but when treated with a large quantity, is partly decomposed, hydrochloric acid being dissolved, and a light milk-white powder separating, which is a basic chloride, or oxychloride, SnCl.SnO + 2HO. Both the crystals and the solution absorb oxygen from the air, and then a basic salt of the sesquioxide is formed which is also insoluble in water. From both these causes, a complete and clear solution of the salt of tin is rarely obtained, unless the water is previously acidulated with hydrochloric acid. This salt is entirely soluble in caustic alkali, but the solution is liable to an ulterior change already mentioned. One part of crystallized protochloride of tin dissolved, together with 3 parts of tartaric acid, in a sufficient quantity of hot water, and carefully neutralized with potash, forms a clear solution, which may be boiled and mixed with any quantity of water without becoming turbid: the white precipitate which forms in it on the addition of a little more potash, especially on heating, is re-dissolved by a larger quantity of potash. (R. Schneider).

When protochloride of tin is heated with a mixture of hydrochloric and sulphurous acids, a yellow precipitate of bisulphide of tin is formed: $6SnCl + 2SO_2 + 4HCl = SnS_2 + 5SnCl_2 + 4HO$. This reaction serves as a test for sulphurous acid.

The protochloride of tin is used in calico-printing, not only as a mordant, but also as a deoxidizing agent, particularly to deoxidize indigo, and to reduce to a lower state of oxidation and discharge the sesquioxides of iron and manganese fixed upon cloth.

Protochloride of tin and potassium; SnCl.KCl. — Protochloride of tin forms a double salt with chloride of potassium, and also with chloride of ammonium, which compounds crystallize in the anhydrous state, and also with 3 eq. of water, or, according to Rammelsberg, with only 1 equivalent.

Anhydrous protochloride of tin fused in ammoniacal gas, absorbs half an equivalent of that gas, according to Persoz, forming $2SnCl.NH_3$, or rather perhaps $SnCl.(NH_3Sn)Cl$.

Protiodide of tin, SnI, is formed by heating a mixture of granulated tin and iodine It is obtained in beautiful shining yellowish red prisms by gently boiling concentrated hydriodic acid with strips of tinfoil in a long glass tube for a day, or more readily by heating the acid with the tin in a sealed glass tube to a temperature of 248°, or at most 302° for an hour; after cooling, the remaining portion of tin is found to be covered with crystals. When tinfoil and iodide of amyl were heated together in a sealed tube for a day to 356°, the tinfoil became covered with yellowish-red quadratic octohedrons at the part where the tube cooled most quickly; but at the part which was immersed in the oil-bath, and therefore cooled more slowly, the metal was covered with sulphur-yellow prisms, which became yellowish-red when taken out (Wöhler). Stannous iodide was found by Boullay, jun., to form double salts with other iodides, particularly with the iodides of the alkaline and earthy metals, in which two atoms of the stannous iodide are combined with one of the other iodide.

Carbonic acid does not combine with either of the oxides of tin.

Protosulphate of tin, $SNO.SO_3$.—Tin dissolves in sulphuric acid, concentrated or a little diluted, yielding a saline mass, which forms a brown solution in water and deposits small crystalline needles on cooling.

Protonitrate of tin, $SNO.NO_5$, is obtained by dissolving hydrated protoxide of tin in nitric acid; the solution cannot be concentrated and is easily altered.

Tartrate of potash and tin, $KO.SnO.(C_8H_4O_{10})$ *or* $C_8H_4(KSn)O_{12}$. — Bitartrate of potash dissolves protoxide of tin, and forms a very soluble salt of potash and tin, which, like most of the tartrates, is not precipitated either by caustic alkalies or by alkaline carbonates. An addition of bitartrate of potash is occasionally made to the solution of tin used in dyeing.

Sesquioxide of tin, Sn_2O_3.—Was obtained by M. Fuchs, by diffusing recently precipitated sesquioxide of iron in a solution of protochloride of tin containing no excess of acid, and afterwards boiling the mixture. A double decomposition occurs, in which sesquioxide of tin precipitates, and protochloride of iron is retained in solution:

$$2SnCl + Fe_2O_3 = Sn_2O_3 + 2FeCl.$$

The sesquioxide thus obtained is a slimy grey matter, and usually yellow from adhering oxide of iron. Ammonia dissolves it easily, and without residue, a character which distinguishes this oxide from the protoxide of tin, the latter being insoluble, or nearly so, in that menstruum. Sesquioxide of tin is dissolved by concentrated hydrochloric acid; the taste of the solution is not metallic. It is distinguished from a salt of the bioxide of tin, by producing the purple precipitate with chloride of gold. A sesquisulphide exists, corresponding with this oxide. The salts of sesquioxide of tin have not been examined.

Bioxide of tin, Stannic oxide, SnO_2, 74·82 *or* 935·25. — This constitutes the common ore of tin, which is generally crystallized. The crystals of *tin-stone* are sometimes brownish-yellow and translucent, at other times dark brown and almost black, and contain small quantities of the protoxides of iron and manganese. Their primitive form is an obtuse octohedron with a square base; their density from 6 92 to 6·96. Bioxide of tin in this state does not dissolve in acids, unless previously ignited with an alkali. Anhydrous stannic oxide may be obtained in colourless crystals derived from a right rhomboïdal prism, which scratch glass, and have a density of 5·72, by decomposing vapour of bichloride of tin with water at a red heat. These crystals are isomorphous with one of the native varieties of titanic acid (brookite), whereas the crystals of native tin-stone are isomorphous with another variety of titanic acid (rutile).

Bioxide of tin is susceptible of two modifications called *stannic* and *metastannic* acid, distinguished from one another by the proportions of water and metallic oxide with which they combine.

Stannic acid, or *Hydrated stannic oxide*, $SnO_2.HO$, is obtained by decomposing bichloride of tin with water, or by precipitating a soluble stannate with an acid. It is white, gelatinous, insoluble in water, but dissolves readily in dilute acids. A moderate heat converts it into metastannic acid. At a red heat, it gives off all its water, and becomes very hard.

Solutions of stannic oxide in acids (the hydrated bichloride for example), are decomposed by *zinc* and *cadmium*, the tin being precipitated in an arborescent form. *Hydrosulphuric acid* and *sulphide of ammonium* throw down the yellow bisulphide soluble in alkalies and in sulphide of ammonium. *Ammonia* throws down a white bulky hydrate, soluble with some turbidity in a large excess of ammonia. The presence of tartaric acid prevents the precipitation. *Potash* throws down a white bulky hydrate (probably containing potash), easily soluble in excess. *Carbonate of potash* gives a white precipitate, consisting, according to Fremy, of stannate of potash, which dissolves in excess of the reagent, but separates completely after a while. *Bicarbonate of potash* and *sesquicarbonate of ammonia* throw down the hydrated oxides, insoluble in excess of the reagent. Chloride of gold gives no precipitate with stannic salts.

All salts of tin are easily reduced to the metallic state when heated on charcoal before the blowpipe with carbonate of soda or cyanide of potassium.

The compounds of stannic acid with bases are represented by the general formula, $MO.SnO_2$. The stannates of the alkalies crystallize readily, and may be obtained in the anhydrous state. They are prepared by dissolving stannic acid in alkalies, or by calcining metastannic acid or the metastannates in contact with an excess of base. *Stannate of potash*, $KO.SnO_2 + 4HO$, is white, very soluble in water, insoluble in alcohol; it crystallizes in oblique rhomboïdal prisms, which are transparent, sometimes very large, and slowly absorb moisture from the air. It has a caustic taste and strong alkaline reaction. Water appears to decompose it after a while into potash and metastannate of potash. It is precipitated from its solution by nearly all soluble salts, even by those of potash, soda and ammonia. *Stannate of soda*, $NaO.SnO_2 + 4HO$, resembles the potash-salt, and is obtained in a similar manner. It crystallizes in hexagonal tables, dissolves in cold more readily than in hot water, is insoluble in alcohol, and has a strong alkaline reaction (Fremy).

The stannates of all other bases are insoluble in water, and may be formed by double decomposition. The sesquioxide of tin may be regarded as a stannate of stannous oxide, $SnO.SnO_2$ (Fremy).

Metastannic acid, SN_5O_{10}. — Tin treated with strong nitric acid is completely transformed into a white powder, which, when dried in the air at ordinary temperatures, contains $Sn_5O_{10}.10HO$; after being heated for some time to 212°, it is reduced to $Sn_5O_{10}.5HO$. It is white, crystalline, insoluble in water, and in dilute nitric acid and sulphuric acid. Monohydrated sulphuric acid dissolves it in considerable quantity, forming a compound which is not decomposed by water or alcohol. It dissolves in dilute hydrochloric acid, forming a liquid, which, when treated with excess of acid, yields a white amorphous precipitate, differing considerably from hydrated bichloride of tin. Metastannic acid also combines with certain organic acids. The acid prepared with nitric acid is completely insoluble in ammonia, but when dissolved in potash and precipitated by an acid, it becomes gelatinous and soluble in ammonia; in that state, it contains more water than in the crystalline state; but by the slightest desiccation, or even by boiling for a few minutes, it gives up part of its water, and is reconverted into the modification insoluble in ammonia. Other hydrates of metastannic acid appear also to exist, possessing different properties.

The *metastannates* are represented by the general formula $(MO.4HO.)Sn_5O_{10}$. They can only exist in the hydrated state, being decomposed when deprived of their basic water. The potash and soda-salts, heated with excess of base, are transformed into stannates. They are soluble in basic water. The other metastannates are insoluble, and are obtained by double decomposition. *Metastannate of potash*, $(KO.4HO).Sn_5O_{10}$, is prepared by dissolving metastannic acid in cold potash; it may be precipitated in the solid state by adding pieces of potash to the liquid. It is gummy, uncrystallizable, and strongly alkaline. At a red heat, it gives off its water and is decomposed; the calcined mass, digested in water, yields up all its alkali and leaves insoluble metastannic acid. The *soda-salt*, $(NaO.4HO)$.

Sn_5O_{10}, closely resembles the potash-salt, but is crystalline, dissolves slowly in water, and is decomposed by boiling water. *Metastannate of stannous oxide*, $(SnO.4HO).Sn_5O_{10}$, is obtained by placing metastannic acid in contact with protochloride of tin. It is yellow, and insoluble in water; when heated in contact with the air, it is transformed into anhydrous stannic acid (Fremy).

Oxide of tin is employed in the preparation of the white glass known as enamel; and the ignited and finely levigated oxide forms *jeweller's putty*, which is used in polishing hard objects. The hydrated oxide resembles alumina in forming insoluble compounds with the organic colouring matters; hence its salts are much prized as mordants.

Bisulphide of tin, *Stannic sulphide*, SnS_2, is precipitated from stannic salts, of a dull yellow colour, by hydrosulphuric acid gas. Prepared in the dry way, by igniting a mixture of stannic oxide, sulphur, and sal-ammoniac in a covered crucible, it forms the *aurum musivum* or *mosaic gold* of the alchemists. In this operation, the sal-ammoniac is indispensable, although it seems to serve no other purpose than to prevent the elevation of temperature which results from the sulphuration. Mosaic gold when well prepared has the yellow colour of gold, and consists of brilliant translucent scales, which are soft to the touch. No acid dissolves it, except aqua-regia. It is decomposed by dry chlorine, yielding the compound, $SnCl_2.SCl_2$.

Bichloride of tin, *Permuriate of tin*, *Stannic chloride*, $SnCl_2$; 129·82 *or* 1622·75.—The anhydrous bichloride of tin, known as the fuming liquor of Libavius, is procured by distilling, at a gentle heat, a mixture of 4 parts of corrosive sublimate and 1 part of tin in filings, or tin amalgamated with a little mercury, and then reduced to powder. A colourless, highly limpid liquid is found in the condenser, which fumes strongly in humid air. The bichloride boils at 248°; the density of its vapour, observed by Dumas, is 9·1997. It forms a solid saline mass with one third of its weight of water, and dissolves in a larger quantity of water. The same salt is obtained in solution, by conducting a stream of chlorine gas into a strong solution of the protochloride of tin, till the latter is saturated, which is shown by the solution ceasing to precipitate mercury from a solution of corrosive sublimate. A solution of this salt extensively used in dyeing, and known as the nitromuriate of tin, is generally prepared by oxidizing crystallized protochloride of tin with nitric acid; or by dissolving tin in a mixture of hydrochloric and nitric acids, avoiding any considerable elevation of temperature.

Ammonio-bichloride of tin, $SnCl_2.NH_3$ *or* $(NH_3Sn)Cl_2$.—Anhydrous bichloride of tin absorbs ammoniacal gas, and forms a white powder, which may be sublimed without decomposition; after sublimation it is entirely soluble in water (Rose).

Chlorosulphide of tin, $SnS_2.2SnCl_2$. — Hydrosulphuric acid gas is rapidly absorbed by bichloride of tin, with formation of hydrochloric acid gas:

$$3SnCl_2 + 2HS = SnS_2.2SnCl_2 + 2HCl.$$

The compound obtained by perfect saturation with hydrosulphuric acid is a yellowish or reddish liquid, heavier than water. When heated, it gives off bichloride of tin, and leaves the bisulphide (Dumas).

Bichloride of tin and sulphur, $SnCl_2.2SCl_2$.—Formed by the action of chlorine gas on bisulphide of tin at ordinary temperatures:

$$SnS_2 + 6Cl = SnCl_2.2SCl_2.$$

Large yellow crystals, which fuse when heated, and sublime without decomposition; they fume in the air more strongly than the bichloride.

Bichloride of tin with Pentachloride of phosphorus, $2SnCl_2.PCl_5$. — When a mixture of the last-described compound with terchloride of phosphorus is moderately heated in a stream of hydrochloric acid gas, a rapid action takes place, and this compound is formed, together with other products:

$$2(SnCl_2.2SCl_2) + 3PCl_3 = 2SnCl_2.PCl_5 + 2PCl_5 + 2S_2Cl.$$

If the retort in which the action takes place is connected with a receiver surrounded with ice, a pasty, yellowish mass collects in the receiver, and an amorphous white body remains in the retort. On heating the yellowish mass to between 212° and 250°, dichloride of sulphur escapes, and there remains a mixture of pentachloride of phosphorus with the double chloride, identical, in fact, with the amorphous white mass in the retort. On heating this mixture to a temperature between 284° and 320°, the pentachloride of phosphorus is also driven off, leaving the double chloride, which sublimes between 392° and 428°, in highly lustrous colourless needles, which, however, soon crumble to an amorphous powder, even when kept in close vessels. The compound fumes strongly in the air, and rapidly absorbs water, being thereby converted into transparent colourless crystals containing water of crystallization.*

Bichloride of tin with Oxychloride of phosphorus, $2SnCl_2 + PO_2Cl_3$. — Obtained by the action of oxychloride of phosphorus on bichloride of tin; if an excess of either substance is present, the compound separates in large isolated crystals. It has a peculiar odour, melts at 131°, and boils at 356°, and distils without alteration if kept from contact with moist air. It fumes in the air and is decomposed by water. When oxychloride of phosphorus comes in contact in a close vessel with the compound, $SnCl_2.2SCl_2$, the whole dissolves, forming a yellowish liquid, from which, after a while, the compound $2SnCl_2.PO_2Cl_3$ crystallizes; and above the crystals there remains a yellow liquid, probably SCl_2 (Casselmann).

Bichloride of tin with Phosphuretted hydrogen, $3SnCl_2.PH_3$. — These two bodies unite without production of hydrochloric acid; the compound is solid (Rose).

Bichloride of tin with potassium, $SnCl_2.KCl$.—The solution of bichloride of tin, when mixed with an equivalent quantity of chloride of potassium and evaporated, yields this double salt in anhydrous regular octohedrons having a vitreous lustre. A similar double salt is formed with chloride of ammonium.

A *sulphate* and *nitrate of bioxide of tin*, have been crystallized; this base forms no carbonate.

Both the *sulphide* and *bisulphide of tin* act as sulphur-acids, combining with alkaline sulphides. The bisulphide of tin dissolves with digestion in sulphide of sodium, and the concentrated solution yields fine crystals of the salt, $2NaS.SnS_2 + 12HO$. By gradually adding tin to melted pentasulphide of sodium, treating the resulting mass with water, and then filtering and evaporating, yellowish octohedral crystals are obtained, containing $NaS.SnS_2 + 2HO$.† The bisulphide of tin is found combined with the subsulphides of copper and iron, forming *tin pyrites*, a rare mineral, $2Fe_2S.SnS_2 + 2Cu_2S.SnS_2$.

Alloys of tin.—Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter, possessing the peculiar whiteness of metallic tin. The most fusible compound of tin and bismuth is that of an atom of each metal, Bi.Sn; it melts at 289·4° (Rudberg). When the metals are mixed in other ratios, a portion first congeals at a higher temperature, separating from the compound mentioned, which remains liquid till the temperature falls to 289·4°. Although tin precipitates copper from its solutions in acids, yet it is possible to precipitate tin upon copper, and to cover the latter with tin, as is proved by the tinning of pins. Tin is dissolved in a mixture of 1 part of bitartrate of potash, 2 of alum, 2 of common salt, and a certain quantity of water, and the pins, which consist of brass wire, are introduced at the boiling temperature. The pins undergo no change in this liquor, supposing it to contain no undissolved tin, but the moment a fragment of tin touches the pins, all those in contact with each other are tinned. Dr. Odling finds that pure copper boiled in a moderately dilute and rather acid solution of stannous chloride, also becomes coated with tin.‡

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* Casselmann. Ann. Ch. Pharm. lxxxiii. 257.

† Kühn, Pogg. Ann. lxxxv. 293.

‡ Chem. Soc. Qu. J. ix. 291.

ESTIMATION OF TIN, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Tin is estimated in the state of bioxide, a compound which contains 78·62 per cent. of the metal. If the tin is united with other metals in the form of an alloy, the alloy must be treated with nitric acid of sp. gr. about 1·3. The tin is then converted into bioxide, while the other metals (with the exception of antimony) are dissolved by the acid. The oxide of tin must then be thoroughly washed, afterwards dried, ignited, and weighed. To insure complete oxidation, the alloy should be finely divided.

When the tin is in solution in hydrochloric acid (which is its usual solvent) it must first be precipitated as a sulphide by hydrosulphuric acid, and the sulphide then converted into bioxide by roasting in an open porcelain crucible, a small quantity of nitric acid being added to insure complete oxidation.

Precipitation by hydrosulphuric acid serves also to separate tin from all metals which are not thrown down by that reagent from their acid solutions.

From *cadmium, copper*, and *lead*, tin may be separated by treating the solution with a slight excess of ammonia, and then adding sulphide of ammonium containing excess of sulphur. All the metals are thereby converted into sulphides; but the sulphide of tin dissolves, while the others are left undissolved.

Volumetric estimation of tin.—The following method of estimating the amount of tin in the commercial protochloride is given by Dr. Penny:[*] it is based on the conversion of protochloride of tin into bichloride by the action of chromic acid in presence of free hydrochloric acid:

$$3SnCl + KO.2CrO_3 + 7HCl = 3SnCl_2 + KCl + Cr_2Cl_3 + 7HO.$$

The solution of the tin-salt is mixed with a sufficient quantity of hydrochloric acid and gently heated, and a solution of bichromate of potash gradually added, till a drop of the liquid added to acetate of lead (a solution of 1 part of that salt in 8 parts of water being scattered in large drops on a porcelain plate) produces a faint yellow colour; or till the liquid produces a dark brown or red colouring in an acidulated mixture of sulphocyanide of potassium and a pure protosalt of iron. With the commercial solution of the protochloride of tin, the contrary method is adopted; that is to say, the tin solution, diluted and reduced to a definite volume, is poured into a solution of bichromate of potash containing a known weight of that salt. Penny finds, by direct experiments, that 83·2 parts of pure bichromate of potash correspond to 100 parts of tin.

SECTION II.

TITANIUM.

Eq. 24·33 *or* 303·7; Ti.

This metal was discovered in 1791, by Mr. Gregor of Cornwall, and afterwards by Klaproth, who gave it the name titanium. In the form of titanic acid it constitutes several minerals, as rutile, anatase, menachanite, &c.; and as titanate of protoxide of iron, it forms ilmenite and other species.

When titaniferous iron-ores are smelted in the blast furnace, small cubic crystals of a bright copper colour are found on the slag which adheres to the lower part of the furnace. These crystals were long supposed to be metallic titanium; but Wöhler[†] has shown that they also contain carbon and nitrogen, being, in fact, a

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[*] Chem. Soc. Qu. J. iv. 249.

[†] Ann. Ch. Pharm. lxxiii. 34; Chem. Soc. Qu. J. ii. 352.

compound of cyanide of titanium with nitride of titanium, $CyTi.3NTi_3$. Pure titanium is obtained by heating the double fluoride of potassium and titanium with potassium in a covered crucible. The metal is then set free with vivid incandescence, and the fluoride of potassium may be removed by washing with water. Titanium thus obtained is a dark green, heavy, amorphous powder, which does not exhibit any shade of copper colour, even after pressure; under the microscope it appears as a cemented mass, having the colour and lustre of iron. Metallic titanium is also obtained by mixing titanic acid with one-sixth of its weight of charcoal and exposing it to the strongest heat of a wind-furnace. It was thus obtained in the form of a copper-coloured or gold-coloured powder by Vauquelin, Lampadius, and others; but possibly the charcoal which they used may have contained nitrogen, and that element united with the reduced metal.

Pure titanium (prepared from the double fluoride) burns with great splendour when heated in the air, and, if sprinkled into a flame, is consumed, with brilliant scintillations, at a considerable distance above the point of the flame. When heated to redness in oxygen-gas, it burns with a splendour resembling a discharge of electricity. In chlorine-gas it exhibits similar phenomena, requiring also the aid of heat to set it on fire. Mixed with red lead and heated, it burns with such violence that the mass is thrown out of the vessel, with loud detonation. Titanium does not decompose water at ordinary temperatures, but on heating the water to the boiling point, hydrogen begins to escape. Warm hydrochloric acid dissolves titanium with brisk evolution of hydrogen. Ammonia added to the solution throws down a black oxide; and, on heating the liquid, hydrogen is evolved, and the precipitate first turns blue, and is afterwards converted into white titanic acid.

Titanium forms three compounds with oxygen: viz., the *protoxide*, TiO, whose composition is, however, doubtful; the *sesquioxide*, Ti_2O_3; and *titanic acid*, TiO_2.

Protoxide of titanium, TiO, 32 33 *or* 403·7 — is formed when titanic acid is exposed in a charcoal crucible, to the highest temperature of a wind-furnace. Where the acid was in contact with the charcoal, a thin coating of metallic titanium is formed; but within, it is changed into a black mass, which is insoluble in all acids, and not otherwise affected by them, and is oxidated with difficulty when heated in contact with air, or by fusion with nitre. Protoxide of titanium is also obtained by the moist way, in the form of a deep purple powder, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid; but it alters so quickly by absorption of oxygen, that no opportunity has yet been obtained of studying its properties. The composition assigned to it above is, therefore, hypothetical. The blue powder is, perhaps, a compound of protoxide of titanium with oxide of zinc or iron.

Sesquioxide of titanium, Ti_2O_3. — When anhydrous titanic acid is strongly ignited in a current of hydrogen gas, it becomes black and loses considerably in weight. From a determination of the actual loss of weight, Ebelmen concludes that sesquioxide of titanium is produced. The residue is not acted upon by nitric or hydrochloric acid, but dissolves in sulphuric acid, forming a violet solution.*

Titanic acid, TiO_2, 40·33 *or* 503·7.—In the mineral rutile, titanic acid is crystallized in the form of tinstone, the link by which tin is connected with titanium. Again, ilmenite and other varieties of titanate of iron, $FeO.TiO_2$ are isomorphous with sesquioxide of iron; and thus tin comes to be connected through titanium with the last order of metals. But titanic acid is dimorphous, and crystallizes, in anatase, in an unconnected form. The best method of obtaining pure titanic acid is to fuse titanate of iron, reduced to powder and levigated with sulphur. The sulphur has no action upon the titanic acid, but converts the protoxide of iron into a sulphide of iron, which is dissolved by hydrochloric acid. If iron is still retained by the titanic acid, the latter is heated in a stream of hydrosulphuric acid

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* Ann. Ch. Phys. [3.] xx. 385.

gas, by which every particle of iron is converted into sulphide, and then removed by hydrochloric acid.

Titanic acid is a white powder, which acquires a yellow tint by exposure to a high temperature; it is infusible and insoluble in water. Titanic acid is considerably analogous in properties to silica; like that acid it has a soluble modification, formed by igniting titanic acid with an alkaline carbonate, which is soluble in dilute hydrochloric acid. The acid solution of titanic acid gives an orange-red precipitate with an infusion of gall-nuts, which is characteristic of titanic acid. On neutralizing the acid solution with ammonia, the soluble modification of titanic acid is thrown down as a white gelatinous precipitate. When this precipitate is dried and heated, it glows, and the titanic acid is then no longer soluble in acids. When a solution of bichloride of titanium, or of the sulphate of titanic acid in water, is boiled for some time, titanic acid precipitates in the insoluble modification.

Titanic acid mixed with borax, or better with phosphorus-salt, forms in the outer blowpipe-flame a colourless glass, but in the inner flame, a glass which is yellow while hot, but assumes a violet colour on cooling. The same character is exhibited by those salts of titanic acid whose bases do not themselves impart any colour to the bead. If the titanic acid contains iron, the colour of the bead is brown-red or blood-red instead of violet. Many titanates yield the blue colour only with phosphorus-salt, not with borax. The colour is produced more readily by heating the substance on charcoal than on platinum wire. The above characters suffice to distinguish titanic acid from all other substances.

Bisulphide of titanium, TiS_2, was discovered by Rose, who formed it by passing the vapour of bisulphide of carbon over titanic acid, in a porcelain tube maintained at a bright red heat.

Bichloride of titanium, $TiCl_2$, was formed by Mr. George, of Leeds, by transmitting chlorine over metallic titanium at a red heat. It is a transparent colourless liquid, resembling bichloride of tin, and boiling a little above 212°. The density of its vapour is 6·615 (Dumas). Bichloride of titanium combines with ammonia, and forms a white saline mass, $TiCl_2.2NH_3$. Metallic titanium is most easily obtained by heating this compound to redness. Bichloride of titanium also absorbs phosphuretted hydrogen, and forms a dry brown powder. From this compound when heated, a lemon-yellow sublimate rises, which Rose found to contain 3 atoms of bichloride of titanium, combined with 1 atom of a compound of phosphuretted hydrogen and hydrochloric acid, analogous to sal-ammoniac, but which could not be isolated. Bichloride of titanium combines with the alkaline chlorides, forming double salts, which are colourless and capable of crystallizing. It also combines with chloride of cyanogen, forming a yellow crystalline compound containing $CyCl.2TiCl_2$, and with anhydrous hydrocyanic acid, forming the compound $HCy.TiCl_2$, a yellow pulverulent substance which sublimes below 212°, in transparent, shining, lemon-yellow crystals.

Bromide of titaninm, $TiBr_2$, is obtained by passing bromine vapour over an intimate mixture of titanic acid and carbon, heated to bright redness, and distilling the resulting brown liquid with excess of mercury to remove free bromine. It is an amber-yellow crystalline body of specific gravity 2·6. It melts at 102°, and boils at 356°. It attracts moisture with the greatest avidity, and is converted into titanic and hydrobromic acids (F. B. Duppa).

A volatile *bifluoride of titanium*, TiF_2, was obtained by Unverdorben, by distilling titanic acid in a platinum apparatus with fluor spar in powder and fuming sulphuric acid.

A definite *sulphate of titanic acid*, $TiO_2 . SO_3$, is obtained by dissolving titanic acid in sulphuric acid, and evaporating to dryness at a heat below redness.

Nitrides of titanium. — H. Rose, by heating the double chloride of titanium and ammonium in ammoniacal gas, or by heating the ammonio-chloride of titanium, $2NH_3 . TiCl_2$, with sodium, obtained a copper-coloured substance which he supposed to be metallic titanium, but which Wöhler has shown to consist of nitride of titanium, Ti_3N_2, or more probably $Ti_6N_4 = 3TiN . Ti_3N$; it contains 28 per cent. of nitrogen. This compound is redder than the cubic crystals of the blast-furnaces, which have a tinge of yellow. Another nitride of titanium, TiN, is produced when titanic acid is strongly heated in a stream of ammoniacal gas. Its powder is dark violet, with a tinge of copper-colour; in small pieces it exhibits a violet copper-colour and metallic lustre. A third nitride, Ti_5N_3, or more probably $2TiN . Ti_3N$, is formed when Rose's titanium is subjected to the action of a stream of hydrogen at a strong red heat. It has a brassy or almost gold-yellow colour and a metallic lustre. It is also obtained (mixed however with carbon) when titanic acid is heated to redness in a stream of cyanogen gas or hydrocyanic acid vapour; no cyanide of titanium is formed in this reaction. All these three nitrides of titanium sustain, without decomposition, a temperature at least equal to that of melting silver. Mixed in the state of powder with the oxides of copper, lead, or mercury, and heated, they emit a lively sparkling flame, and reduce the oxides to the metallic state. When fused with hydrate of potash, they give off ammoniacal gas (Wöhler).

Nitrocyanide of titanium, $C_2NTi . 3Ti_3N$. — This is the copper-coloured compound already spoken of as occurring in the iron furnaces, and formerly mistaken for metallic titanium. Its formation appears to be connected with that of cyanide of potassium, so constantly observed in the blast-furnaces. It sometimes occurs in very large masses; in a furnace at Rübeland in the Hartz, a mass of it was found, weighing 80 pounds. This compound forms cubic crystals harder than quartz, and of specific gravity 5·3. It contains 18 per cent. of nitrogen and 4 of carbon. In its chemical characters, it resembles the nitrides just described, giving off ammonia when heated with potash, and reducing the oxides of lead, copper, and mercury, when heated with them. A similar product may be formed by placing a mixture of titanic acid and ferrocyanide of potassium in a well closed crucible, and exposing it for an hour to a heat sufficient to melt nickel (Wöhler).

ESTIMATION OF TITANIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Titanium is always estimated in the form of titanic acid. This compound is best precipitated from its solutions in acids by ammonia, which throws it down in the form of a very bulky precipitate, resembling hydrate of alumina. A great excess of ammonia must be avoided, as it would re-dissolve a small portion of the titanic acid. The precipitate after ignition contains 60 per cent. of titanium.

If the titanic acid, after precipitation by ammonia, is to be redissolved in acids, which is sometimes necessary in order to separate it from other metals, great care must be taken in the precipitation to avoid all rise of temperature, and the precipitate must be washed with cold water, because heat has the effect of rendering titanic acid more or less insoluble in acids.

Titanic acid may also in some cases be separated from its acid solutions by boiling; from the solution in sulphuric acid, complete precipitation is effected by this method; but when hydrochloric acid is the solvent, a small portion of titanic acid always remains in solution after boiling.

Protoxide of titanium is precipitated from its solutions by ammonia, and the precipitate, after standing from 24 to 36 hours, is converted, with evolution of hydrogen, into titanic acid, in which form it may be estimated.

From the *alkalies* and *alkaline earths*, titanic acid may be separated by ammonia, the solution in the latter case being carefully excluded from the air. Baryta may also be separated by sulphuric acid.

Titanic acid is separated from *magnesia* by boiling, if the two are dissolved in sulphuric acid, and by precipitation with carbonate of baryta, when hydrochloric acid is the solvent.

The separation from *alumina* and *glucina* is also effected by boiling the sulphuric acid solution.

From the metals which are precipitated as sulphides by sulphide of ammonium, viz., *manganese, iron, cobalt, nickel,* and *zinc,* titanic acid is separated by mixing the acid solution with tartaric acid and excess of ammonia (which then forms no precipitate), and adding sulphide of ammonium, which precipitates everything but the titanic acid. The filtered solution is then evaporated to dryness, and the residue ignited in a platinum crucible to expel ammoniacal salts and burn away the carbon of the tartaric acid. As this carbonaceous matter is very difficult to burn, the ignition should either be performed in a muffle furnace, or a stream of oxygen should be very gently directed into the crucible. The residue consists of titanic acid, which may then be weighed.

From *cadmium, copper, lead,* and *tin,* titanium is easily separated by hydrosulphuric acid.

SECTION III.

CHROMIUM.

Eq. 26·8 *or* 335; Cr.

This metal, so remarkable for the variety and beauty of its coloured preparations, was discovered by Vauquelin in 1797, in the red mineral now known as chromate of lead. It has since been found in other minerals, more particularly *chrome-iron* ($FeO . Cr_2O_3$), a mineral which many countries possess in considerable quantity. It is from this ore that the compounds of chromium, used in the arts, are actually derived. The metal may be procured by the reduction of its oxide, in the usual way; but the reduction is as difficult as that of manganese. Chromium is a greyish-white metal, of density 5·9, very difficult to fuse, and not magnetic. It does not undergo oxidation in the air. It dissolves in hydrofluoric acid with evolution of hydrogen. Chromium is also obtained as a brown powder, when sesquichloride of chromium is heated in ammoniacal gas (Liebig).

Chromium forms several compounds with oxygen; viz. *protoxide of chromium,* or *chromous oxide,* CrO, isomorphous with ferrous oxide, &c.; *sesquioxide of chromium,* or *chromic oxide,* Cr_2O_3, isomorphous with ferric oxide and alumina; and *chromic acid,* CrO_3, isomorphous with sulphuric acid; also a *chromoso-chromic oxide,* Cr_3O_4, or $CrO.Cr_2O_3$, and four oxides intermediate between chromic oxide and chromic acid, which may, in fact, be regarded as chromates of chromic oxide; viz. *monochromate of chromic oxide,* or $Cr_2O_3.CrO_3 = Cr_3O_6$; the *bichromate,* $Cr_2O_3.2CrO_3 = Cr_4O_9$; the neutral chromate, $Cr_2O_3.3CrO_3 = Cr_5O_{12}$, and the acid chromate, $Cr_2O_3.4CrO_3 = Cr_6O_{15}$.

Protoxide of chromium, Chromous oxide, CrO; 34·8 or 435.—This oxide probably exists in chrome-iron, and in pyrope. It is precipitated in the form of a hydrate by the action of potash on a solution of the protochloride. The anhydrous protoxide has not yet been obtained. The hydrate is very unstable, decomposes water, even at ordinary temperatures, and if the air be not excluded by filling the apparatus with hydrogen is converted, almost as soon as formed, into chromoso-chromic oxide, Cr_3O_4, with evolution of hydrogen (Péligot). It is yellow when recently precipitated, brown when dry, and may be preserved unaltered in dry air. When ignited it gives off hydrogen, and the oxygen thereby liberated converts the remaining protoxide into sesquioxide (Moberg).

Hydrated chromous oxide is insoluble in dilute acids, but dissolves slowly in strong acids. The chromous salts are best prepared by mixing a solution of the protochloride with the corresponding potash or soda salts, access of air being carefully prevented. They are generally of a red colour, sometimes inclining to blue;

dissolve but sparingly in cold water, but more readily in hot water. Like ferrous salts, they dissolve large quantities of nitric oxide, forming dark brown solutions.

Protochloride of chromium, chromous chloride, CrCl; 62·3 *or* 778·75. — Obtained by passing hydrogen gas over perfectly anhydrous sesquichloride of chromium very gently heated, as long as hydrochloric acid gas continues to escape. The hydrogen must be previously freed from all traces of oxygen by passing it through a solution of protochloride of tin in caustic potash, then through tubes containing sulphuric acid and chloride of calcium, and lastly over red-hot metallic copper. The protochloride is also formed by passing dry chlorine gas over a red-hot mixture of charcoal and chromic oxide. The first method yields the protochloride in the form of a white, velvety substance, retaining the form of the sesquichloride from which it has been formed; the second method yields it in fine white crystals, usually mixed, however, with chromic oxide, chromic chloride, and charcoal.

Protochloride of chromium dissolves in water, with evolution of heat, forming a blue solution, which rapidly turns green when exposed to the air or to chlorine gas. With *potash* it forms a dark brown precipitate (yellow, according to Moberg, if the air be completely excluded) of hydrated chromous oxide, which, however, quickly changes to light brown chromoso-chromic oxide, with evolution of hydrogen. *Ammonia* forms a greenish white precipitate, without evolution of hydrogen. With ammonia and sal-ammoniac, a blue liquid is formed which turns red on exposure to the air. *Sulphide of ammonium* or *potassium* forms a black precipitate of chromous sulphide. The solution of protochloride of chromium is one of the most powerful deoxidizing agents known. With a solution of *monochromate of potash*, it forms a dark brown precipitate of chromoso-chromic oxide, which, however, disappears on the addition of an excess of the protochloride, and forms a green solution. It precipitates *calomel* from a solution of corrosive sublimate. With *cupric salts*, it forms at first a white precipitate of cuprous chloride; but when added in excess throws down red cuprous oxide. It instantly converts *tungstic acid* into blue oxide of tungsten, and precipitates *gold* from the solution of the chloride.

Chromous carbonate is formed by adding a solution of the chloride to carbonate of potash; its precipitate is red or red-brown, if the alkaline solution is hot, but in the form of dense yellow or bluish green flakes, if it is cold; the precipitate appears, however, to have the same composition in all cases (Moberg).

Chromous sulphite is obtained by double decomposition in the form of a brick-red precipitate, which becomes bluish green on exposure to the air (Moberg).

Chromous sulphate. — When the metallic powder obtained by treating sesquichloride of chromium with potassium is treated with dilute sulphuric acid, hydrogen is evolved, and a solution obtained which exhibits the characters of a chromous salt (Péligot).

Chromoso-chromic oxide, $Cr_3O_4 = CrO.Cr_2O_3$. — Formed when the protoxide comes in contact with water, and consequently at the moment of its precipitation by potash, from a solution of the protochloride. After washing with water and drying in vacuo, it has the colour of Spanish tobacco. It is but feebly attacked by acids. The hydrate is composed of $Cr_3O_4.HO$; when heated, it is converted into chromic oxide with evolution of hydrogen.

Sesquioxide of chromium, Chromic oxide, 77·6 or 970. — This oxide exists in chrome-iron, but is not immediately derived from that mineral. When chromate of mercury, the orange precipitate obtained on mixing nitrate of mercury and chromate of potash, is strongly ignited, chromic oxide remains as a powder of a good green colour. Chromic oxide is also obtained, by deoxidizing the chromic acid of bichromate of potash in various ways; by ignition with sulphur, for instance, or by igniting together 1 part of bichromate of potash with 1½ parts of sal-ammoniac and 1 part of carbonate of potash, whereby chloride of potassium and sesquioxide of chromium are formed, the chromic acid losing half its oxygen, which is converted into water by the hydrogen of the ammonia. Another process, interesting from affording the oxide in the state of crystals, is to pass the vapour of chlorochromic acid (CrO_2Cl) through a tube heated to whiteness, when oxygen and chlorine gases are disengaged, and chromic oxide attaches itself to the surface of the tube. The crystals have a metallic lustre, and are of so deep a green as to appear black; they have the same form as specular iron ore, a density of 5·21, and are as hard as corundum (Wöhler). The ignited oxide is not soluble in acids; heated with access of air, and in contact with an alkali, it absorbs oxygen, and is converted into chromic acid. Fused with borax or other vitreous substances, sesquioxide of chromium produces a beautiful green colour; it is the colouring matter of the emerald, and is employed to produce a green colour upon earthenware. Sesquioxide of chromium (and not chromic acid) is also the colouring matter of *pink colour* applied to stoneware. This substance is formed by strongly igniting a mixture of 100 parts of bioxide of tin, 33 parts of chalk, and not more than one part of sesquioxide of chromium.*

To obtain the same oxide in the hydrated state, a solution of bichromate of potash is brought to the boiling point, and hydrochloric acid and alcohol added alternately in small quantities, till the solution passes from a red to a deep green colour, and no longer effervesces from escape of carbonic acid gas, on addition of either the acid or alcohol. In this experiment, the chromic acid liberated by the hydrochloric acid, is deprived of half its oxygen by the hydrogen and carbon of the alcohol, and the resulting sesquioxide of chromium is dissolved by the excess of hydrochloric acid present, and in fact converted into the corresponding sesquichloride of chromium. Many other organic substances may be used in place of alcohol in this experiment, such as sugar, oxalic acid, &c. The reduction may also be effected by hydro-sulphuric acid or even by hydrochloric acid alone, if added in sufficient excess; in this last case, sesquichloride of chromium and chloride of potassium are then formed, and part of the chlorine escapes as gas; thus:

$$KO.2CrO_3 + 7HCl = KCl + Cr_2Cl_3 + 7HO + 3Cl.$$

The oxide of chromium is precipitated from the green solution by ammonia, and falls as a pale bluish-green hydrate. The same oxide is obtained more directly, when to a boiling solution of bichromate of potash a hot solution of pentasulphide of potassium is added, the chromic acid then giving half its oxygen to the sulphur.

Hydrated chromic oxide is soluble in acids, and forms salts. It is also dissolved by potash and soda, but not to a great extent by ammonia. Its salts have a sweet taste, and are poisonous. The oxide itself becomes of a greener colour when dried, and loses water. A moderate heat affects its relations to acids, the sulphate of the heated (or green) oxide not forming a double salt, for instance, with sulphate of potash. When heated to redness, it glows, or undergoes the same change as zirconia, bioxide of tin, and many other hydrated oxides when made anhydrous; becomes denser, assumes a pure green colour, and ceases to be soluble in acids.

The salts of chromic oxide exhibit two different modifications, green and violet; some acids, *e.g.*, sulphuric and hydrochloric, produce both modifications; others only one. *Ammonia* produces, in solutions of green salts, a bluish-grey precipitate, but in solutions of the violet salts, a greenish-grey precipitate, both of which, however, yield green solutions when dissolved in sulphuric or hydrochloric acid (Regnault); according to H. Rose, however, the precipitate is bluish-grey in both cases. The liquid above the precipitate has a reddish colour, and contains a small quantity of chromic acid. *Potash* and *soda* form similar precipitates, which dissolve in excess of the alkali, forming green solutions from which the chromic oxide is precipitated by boiling. The *alkaline carbonates* form greenish

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* Malaguti, Ann. Ch. Phys. [3.] lxi. p. 433. Mr. O. Sims finds that sesquioxide of iron and bioxide of manganese may be substituted for oxide of chromium in pink colour, so that the coloration of that substance is of a very peculiar character.

precipitates (violet by candle-light), which dissolve to a considerable extent in excess of the reagent. *Hydrosulphuric acid* forms no precipitate; *sulphide of ammonium* throws down the hydrated sesquioxide.

Zinc, immersed in a solution of chrome-alum or sesquichloride of chromium excluded from the air, gradually reduces the chromic salt to a chromous salt, the liquid after a few hours acquiring a fine blue colour, and hydrogen being evolved by decomposition of water. If the zinc be left in the liquid after the change of colour from green to blue is complete, hydrogen continues to escape slowly, and the liquid after some weeks or months, is found no longer to contain chromium, the whole of that metal being precipitated in the form of a basic salt, and its place taken by zinc. *Tin*, at a boiling heat, likewise reduces the chromic salt to a chromous salt, but only to a limited extent; and on leaving the liquid to cool after the action has ceased, a contrary action takes place, the protochloride of chromium decomposing the protochloride of tin previously formed, reducing the tin to the metallic state, and being itself reconverted into sesquichloride. *Iron* does not reduce chromic salts to chromous salts, but merely precipitates a basic sulphate of chromic oxide, or an oxychloride, as the case may be.*

Sesquioxide (and also the protoxide) of chromium, ignited with an alkaline carbonate, or better with a mixture of the carbonate and nitre, is converted into chromic acid, which unites with the alkali; and on dissolving the fused product in water, filtering if necessary, and neutralizing with acetic acid, the characteristic reactions of chromic acid (p. 511) may be obtained with lead and silver-salts. An oxide of chromium fused with borax, in either blowpipe flame, yields an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart decided colours to the bead.

A *sesquisulphide of chromium*, Cr_2S_3, corresponding with the oxide, is obtained by exposing the latter, in a porcelain tube, to the vapour of bisulphide of carbon, at a bright red heat. It is a substance of a dark grey colour, which is dissolved by nitric acid.

Sesquichloride of chromium, Chromic chloride, Cr_2Cl_3; 160·1 or 2001.2.—This salt is obtained as a sublimate of a peach-purple colour, when chlorine is passed over a mixture of oxide of chromium and charcoal, ignited in a porcelain tube: or in the hydrated state by evaporating the solution of sesquichloride of chromium to dryness. The salt obtained by the latter process is a green powder containing Cr_2Cl_3+9HO. When heated, it gives off water and hydrochloric acid, and leaves a residue of oxychloride of chromium. Heated in a current of hydrochloric acid gas, it likewise parts with its water, and is converted into the violet anhydrous sesquichloride. The solution, evaporated in vacuo, leaves an amorphous mass which dissolves in water with evolution of heat, and consists of Cr_2Cl_3+6HO (Péligot). Anhydrous sesquichloride of chromium is perfectly insoluble in cold water, and dissolves but very slowly in boiling water; but if to cold water in which the sesquichloride is immersed, there be added a very small quantity, even $\frac{1}{10000}$, of protochloride of chromium, a green solution is formed identical with that which is obtained by dissolving chromic oxide in hydrochloric acid (Péligot).

Chromic sulphate, $Cr_2O_3.3SO_3$; 197·6 or 247·0. — Chromic oxide is dissolved by sulphuric acid, but the salt does not crystallize. Chromic sulphate exhibits a violet and a green modification. The violet sulphate is obtained by leaving 8 parts of hydrated chromic oxide, dried at 212°, and 8 or 10 parts of strong sulphuric acid in a loosely stoppered bottle for several weeks. The solution, which is green at first, gradually becomes blue, and deposits a greenish blue crystalline mass. On dissolving this substance in water, and adding alcohol, a violet-blue crystalline precipitate is formed; and by dissolving this precipitate in very weak alcohol, and leaving the solution to itself for some time, small regular octohedrons are deposited, containing $Cr_2O_3 . 3SO_3+15HO$. The *green sulphate* is prepared

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* H. Loewel, Ann. Ch. Phys. [3], xl. 42.

by dissolving chromic oxide in strong sulphuric acid at a temperature between 122° and 140°; also by boiling a solution of the violet sulphate. The liquid, when quickly evaporated, yields a green crystalline salt, having the same composition as the violet sulphate. The green sulphate dissolves readily in alcohol, forming a blue solution, but the violet salt is insoluble in alcohol. The solution of the green sulphate is not completely decomposed by soluble baryta-salts at ordinary temperatures, a boiling heat being required to complete it; the violet sulphate, on the contrary, is deprived of all its sulphuric acid by baryta-salts at ordinary temperatures. When either the green or the violet sulphate is heated to 390°, with excess of sulphuric acid, a light yellow mass is obtained, which, when further heated, leaves a residue of anhydrous chromic sulphate, having a *red* colour. This anhydrous salt is completely insoluble in water, and dissolves with difficulty even in acid liquids.*

Chromic sulphate forms a crystallizable double salt with sulphate of potash, viz., *chrome-alum*, $KO.SO_3 + Cr_2O_3.3SO_3 + 24HO$. This salt is produced when a mixture of its constituent salts, with a little free sulphuric acid, is left to spontaneous evaporation. The best mode of preparing it is to mix three parts of a saturated solution of neutral chromate of potash, first with one part of oil of vitriol, and then with two parts of alcohol, which is to be added by small portions to the mixture of acid and chromate, and not to apply artificial heat. The chromic acid is thus deoxidized in a gradual manner, and large crystals of the double sulphate are slowly deposited (Fischer). The octohedral crystals of chrome-alum are of a dark purple colour, and of a beautiful ruby-red, when so small as to be transparent. The solution is bluish-purple, but when heated to 140° or 180° becomes green, and, according to Fischer, either deposits on evaporation a bright-green amorphous, difficultly soluble mass, or yields crystals of sulphate of potash, while green chromic sulphate remains in solution. According to Loewel,† on the contrary, the change of the purple into the green salt does not arise from a separation of the two simple salts, but merely from loss of water of crystallization. A solution of chrome-alum, which has become green and uncrystallizable by heating, does not deposit any sulphate of potash even when concentrated; neither does that salt separate when the crystals are melted in a sealed tube; but the green liquid obtained by either of these processes yields, when heated to 77° and 86° in a dry atmosphere, a dark green mass containing $Cr_2O_3.3SO_3 + KO.SO_3$, with scarcely 6 eq. water (Loewel). The violet crystals containing 24 Aq., when left for several days in dry air at a temperature between 77° and 86°, give off 12 Aq., and assume a lilac colour. At 212°, another quantity of water goes off, and the crystals become green; and, by gradually raising the temperature to about 660°, the whole of the water may be expelled without causing the salt to melt. The anhydrous crystals are green, and dissolve without residue in boiling water, but at a temperature somewhat above 660°, they suddenly become greenish-yellow, without perceptible loss of weight, and are afterwards perfectly insoluble in water.

Oxalate of chromium and potash, $3(KO.C_2O_3) + Cr_2O_3.3C_2O_3 + 6HO$.—This is another beautiful double salt of chromium. It is easily prepared by the following process of Dr. Gregory:—One part of bichromate of potash, two parts of binoxalate of potash, and two parts of crystallized oxalic acid are dissolved together in hot water. A copious evolution of carbonic acid gas takes place, arising from the deoxidation of the chromic acid, at the expense of a portion of the oxalic acid; and nothing fixed remains, except the salt in question, of which a pretty concentrated solution crystallizes upon cooling in prismatic crystals, which are black by reflected light, but of a splendid blue by transmitted light, when sufficiently thin to be translucent. The oxide of chromium is not completely precipitated from this salt by an alkaline carbonate; and it is remarkable that only a small portion of the oxalic acid is thrown down from it by chloride of calcium. When fully dried and then carefully ignited, this salt is completely decomposed,

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* Regnault, Cours de Chimie.

† Ann. Ch. Phys. [3], xliv. 313.

and leaves a mixture of chromate and carbonate of potash. The corresponding double oxalate of chromium and soda contains 9HO, according to Mitscherlich. In the analogous oxalate of ferric oxide and soda, the proportion of water appeared to the author to be 10HO.

The mineral *chrome-iron*, $FeO.Cr_2O_3$, crystallizes in octohedrons, and corresponds with the magnetic oxide of iron, having the sesquioxide of iron replaced by sesquioxide of chromium. Its density is 4·5; it is about as soft as felspar, and infusible. When exposed to long-continued calcination, in contact with carbonate of potash, in a reverberatory furnace, the oxide of chromium of this compound absorbs oxygen, and combines as chromic acid with the potash, while the protoxide of iron becomes sesquioxide. The addition of nitre increases the rapidity of oxidation, but is not absolutely required in the process. A yellow alkaline solution of carbonate and chromate of potash is obtained by lixiviating the calcined matter, which is generally converted into the red chromate or bichromate of potash, by the addition of the proper quantity of sulphuric acid, the latter salt being more easily purified by crystallization than the neutral chromate.

Chromic acid, CrO_3, 52·19 *or* 651·8.—This acid is not liberated from the chromates in a state of purity by any acid except the fluosilicic; it is also easily altered. Fluosilicic acid gas is conducted into a warm solution of bichromate of potash, till the potash is completely separated as the insoluble fluoride of silicon and potassium, which may be ascertained by testing a few drops of the solution with tartaric acid or chloride of platinum. The solution is evaporated to dryness by a steam heat, and the chromic acid redissolved by water; it gives an opaque, dull red solution. Chromic acid may also be obtained anhydrous and in acicular crystals, by distilling, in a platinum retort, a mixture of 4 parts of chromate of lead, 3 parts of finely pulverized fluor spar, and 7 parts of Nordhausen sulphuric acid; sulphate of lime is formed, together with perfluoride of chromium, the vapour of which is received in a large platinum crucible, covered with wet paper and used as a condenser. The perfluoride is decomposed by the aqueous vapour from the paper, being resolved into hydrofluoric acid and beautiful orange-red acicular crystals of chromic acid, which fill the crucible. A third and easier method of preparing chromic acid is to mix a solution of bichromate of potash, saturated between 122° and 140°, with $1\frac{1}{2}$ times its volume of strong sulphuric acid, adding the acid by successive small portions. Bisulphate of potash is then formed, which remains in solution, and the liquid, as it cools, deposits the chromic acid in long red needles. These may be drained, first in a funnel, afterwards on a brick; then dissolved in water; the solution treated with a small quantity of chromate of baryta to remove the last portion of sulphuric acid; and the filtered liquid evaporated in vacuo. Chromic acid differs remarkably from sulphuric acid, in having but little affinity for basic water, so that it may be obtained anhydrous by evaporating its solution to dryness. Indeed, the chromate of water is not known to exist, even in combination, both the bichromate and terchromate of potash being anhydrous salts. The free acid is a powerful oxidizing agent, and bleaches organic colouring matters: chromic acid then loses half its oxygen, and becomes oxide of chromium. It is also converted into sesquichloride of chromium by hydrochloric acid, with evolution of chlorine:

$$2CrO_3 + 6HCl = Cr_2Cl_3 + 6HO + 3Cl;$$

and into sesquioxide by hydrosulphuric acid, with precipitation of sulphur:

$$2CrO_3 + 3HS = Cr_2O_3 + 3HO + 3S.$$

Sulphurous acid passed through a solution of chromic acid, or its salts, throws down a brown precipitate, consisting of monochromate of chromic oxide, or bioxide of chromium; $Cr_2O_3.CrO_3 = 3CrO_2$. The other intermediate oxides, or chromates of chromic oxide mentioned on page 505, are formed by other imperfect reductions of chromic acid, or by the imperfect oxidation of chromic oxide.

They are all brown substances, soluble in potash and in nitric acid. One of them, the bichromate, dissolves also without decomposition in hydrochloric and sulphuric acid; the others are reduced by hydrochloric acid to sesquichloride, with evolution of chlorine, and resolved by sulphuric acid into chromic acid and sulphate of chromic oxide.*

Chromic acid forms bibasic, monobasic, biacid, and a few tri-acid salts. The monochromates of the alkalies are yellow, the bichromates red; the chromates of the metals proper are bright yellow, red, or occasionally of some other colour. All chromates heated with oil of vitriol give off oxygen, and form sulphate of chromic oxide, together with another sulphate. When heated with hydrochloric acid, they give off chlorine and form sesquichloride of chromium, together with another metallic chloride. Heated in the anhydrous state with common salt and sulphuric acid, they give off red vapours of chlorochromic acid, which condense to a brownish red liquid. Similarly, when heated with fluor spar and sulphuric acid, they give off red vapours of terfluoride of chromium. A few only of the chromates, more particularly those of the alkalies, are soluble in water, but they all dissolve in nitric acid. Solutions of the alkaline chromates form a pale yellow precipitate with baryta salts; bright yellow with lead-salts; brick red with mercurous salts; and crimson with silver salts.

Chromate of potash, Yellow chromate of potash, $KO.CrO_3$; 97·8 or 1222·5.—This salt is produced in the treatment of the chrome ore, but is seldom crystallized. It may be formed from the bichromate, by fusing that salt with an equivalent quantity of carbonate of potash; or by adding caustic potash to a red solution of the bichromate, till its colour becomes a pure golden yellow. The solution of chromate of potash has a great tendency to effloresce upon the sides of the basin when evaporated. Its crystals are of a yellow colour, anhydrous, and isomorphous with sulphate of potash. One hundred parts of water at 10° dissolve 48½ parts of this salt; the solution preserves its yellow colour, even when diluted to a great degree.

Bichromate of potash, Red chromate of potash, $KO.2CrO_3$; 148·6 or 1857·5.—This beautiful salt, of which a large quantity is consumed in the arts, crystallizes in prisms or in large four-sided tables, of a fine orange-red colour. It fuses below a red heat, and forms on cooling a crystalline mass, the crystals of which have, according to Mitscherlich, the same form as those obtained from an aqueous solution; but this mass falls to powder as it cools, from the unequal contraction of the crystals in different directions. At 60°, water dissolves $\frac{1}{10}$ of its weight of this salt, and at the boiling point a considerably greater quantity.

Bichromate of chloride of potassium, Péligot's salt, $KCl.2CrO_3$.—This salt, which we are obliged to designate as if it contained chloride of potassium combined as a base with chromic acid, is formed by dissolving together, with the aid of heat, about three parts of bichromate of potash and four of concentrated hydrochloric acid, with a small quantity of water, avoiding the evolution of chlorine. It crystallizes in flat red quadrangular prisms, and is decomposed by solution in pure water.

Terchromate of potash, $KO.3CrO_3$, is obtained crystallized when a solution of the bichromate is mixed with nitric acid, and evaporated. Bichromates of soda and silver exist which are anhydrous, like the bichromate of potash (Warington).

Chromate of soda, $NaO.CrO_3 + 10HO$.—By the evaporation of a concentrated solution of this salt, it is obtained in large fine crystals, having the form of glauber salt. The bichromate crystallizes in thin, hyacinth-red, six-sided prisms, bevelled at the ends.

Chromate of ammonia, $NH_4O.CrO_3$ is prepared by evaporating a mixture of chromic acid with a slight excess of ammonia. It crystallizes in lemon-yellow

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* For a full account of these brown oxides, see the translation of Gmelin's Handbook, iv. 113.

needles, very soluble in water, and having an alkaline reaction and pungent saline taste. When heated, they give off ammonia, water, and oxygen, and leave sesquioxide of chromium. The *bichromate*, $NH_4O.2CrO_3$, forms orange-yellow or reddish brown rhombic tables, which at a heat below redness are decomposed, with emission of light and feeble detonation, leaving the sesquioxide. It combines with chloride of mercury, forming crystalline compounds, containing $NH_4O.2CrO_3.HgCl + HO$, and $3(NH_4O.2CrO_3).HgCl$ (Richmond and Abel).* Rammelsberg has obtained an acid salt composed of $NH_4O.6CrO_3 + 10HO$.

Chromate of baryta, $BaO.CrO_3$ is a lemon-yellow powder obtained by precipitating a baryta-salt with an alkaline chromate. It is insoluble in water, but dissolves easily in nitric, hydrochloric, or chromic acid. When a baryta-salt is precipitated with neutral chromate of potash, and sulphuric acid added, the precipitate dissolves with partial decomposition, and on diluting with water, mixing the filtered solution with chromic acid, and evaporating in vacuo, neutral chromate of baryta first separates, then crystals of a *bichromate*, $BaO.2CrO_3 + 2HO$, and afterwards a double salt containing $2(BaO.3CrO_3.HO) + (KO.3CrO_3.HO)$. (Bahr.)†

Neutral chromate of lime, $CaO.CrO_3$, is obtained by treating carbonate of lime with aqueous chromic acid; and by treating the neutral salt with excess of chromic acid and evaporating, a *bichromate*, $CrO.2CrO_3 + 2HO$, is obtained. Chloride of calcium mixed with monochromate of potash, yields a double salt containing $5(CaO.CrO_3) + KO.CrO_3$. (Bahr.)

Chromate of magnesia forms, according to the author's observations, yellow crystals which are very soluble, and contain 5HO. It does not form a double salt with chromate of potash, as sulphate of magnesia does with sulphate of potash. It is remarked that the insoluble metallic chromates generally carry down portions of the neutral precipitating salts, or of subsalts, and their analysis is often unsatisfactory from that cause. When the magnesian chromates are compared with the sulphates of the same family, the former are found to have their water readily replaced by metallic oxides, but not by salts; so that subchromates with excess of oxide are numerous, while few or no double chromates exist.

Chromate of lead, $PbO.CrO_3$; 162·4 or 2030.—This compound, so well known as *chrome-yellow*, is obtained by mixing nitrate or acetate of lead with chromate or bichromate of potash. The precipitate is of a lighter shade from dilute than from concentrated solutions. It is entirely soluble in potash or soda, but not in dilute acids.

Subchromate of lead, $2PbO.CrO_3$, is of a red colour. It is formed when a solution of neutral chromate of potash, mixed with as much free alkali as it already contains, is added to a solution of nitrate of lead. But the finest vermilion-red subchromate is formed when one part of the neutral chromate of lead is thrown into five parts of nitre in a state of fusion by heat. Water dissolves the chromate and nitrate of potash in the fused mass, and leaves the subchromate of lead as a crystalline powder, (Liebig and Wöhler). An orange pigment may be obtained very economically, by boiling the sulphate of lead, which is a waste product in making acetate of alumina from alum by means of acetate of lead, with a solution of chromate of potash. The subchromate of lead forms a beautiful orange upon cloth, which is even more stable than the yellow chromate, not being acted upon by either alkalies or acids. One method of dyeing chrome-orange, is to fix the yellow chromate of lead first in the calico, by dipping it successively in acetate of lead and bichromate of potash, and then washing it. This should be repeated, in order to precipitate a considerable quantity of the chromate in the calico. A milk of lime is then heated in an open pan; and when it is at the point of ebullition, the yellow calico is immersed in it, and instantly becomes orange, being deprived of a portion of its chromic acid by the lime, which forms a soluble chromate of

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* Chem. Soc. Qu. J. iii. 139.

† J. pr. Chem. lx. 60.

lime. At a lower temperature, lime-water dissolves the chromate of lead entirely, and leaves the cloth white.

Chromate of silver falls as a reddish brown precipitate when nitrate of silver is added to neutral chromate of potash. Dissolved in hot and concentrated solution of ammonia, it yields, on cooling, large well formed crystals, $AgO.CrO_3 + 2NH_3$, isomorphous with the analogous ammoniacal sulphate and seleniate of silver.

Chlorochromic acid, CrO_2Cl, or $2CrO_3.CrCl_3$.—This is a volatile liquid, obtained by distilling, in a glass retort, at a gentle heat, 3 parts of bichromate of potash and 3½ parts of common salt, previously reduced to powder and mixed together, with 5 parts by water-measure of oil of vitriol, discontinuing the distillation when the vapours, from being of a deep orange-red, become pale — that change arising from watery vapour. The compound is a heavy red liquid, decomposed by water. The density of its vapour is 5·9.

Terfluoride of chromium, CrF_3, is obtained in the manner already mentioned under the preparation of chromic acid. It is a blood-red liquid. No corresponding terchloride of chromium has been obtained in an isolated state.

Perchromic acid, Cr_2O_7. — When peroxide of hydrogen dissolved in water is mixed with a solution of chromic acid, the liquid assumes a deep indigo-blue colour, but often loses this colour very rapidly, giving off oxygen at the same time. The same blue colour is formed by adding a mixture of aqueous peroxide of hydrogen and sulphuric or hydrochloric acid to bichromate of potash; but, in a very short time, oxygen is evolved, and a potash-salt, together with a chromic salt, left in solution. For each atom of $KO.2CrO_3$, four atoms of oxygen are evolved, provided an excess of HO_2 be present:

$$KO.2CrO_3 + O + 4SO_3 = KO.SO_3 + Cr_2O_3.3SO_3 + 4O.$$

The peroxide of hydrogen first gives up 1 at. O to the 2 at. of CrO_3, and forms Cr_2O_7; and this compound is subsequently resolved into Cr_2O_3 and 4O. With ether, perchromic acid forms a more stable blue mixture than with water, and in this state may be made to unite with ammonia and with certain organic bases, forming very stable compounds, from which stronger acids separate the blue acid.

ESTIMATION OF CHROMIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Chromium is usually estimated in the state of sesquioxide. When it exists in solution in that state, it may be precipitated by ammonia, care being taken to avoid a large excess of that reagent (which would dissolve a portion), and to heat the liquid for some time. The chromic oxide is then completely precipitated, and the precipitate, after washing and drying, is reduced by ignition to the state of anhydrous sesquioxide, containing 70·1 per cent. of the metal.

When chromium exists in solution in the state of chromic acid, it is best to precipitate it by a solution of mercurous nitrate; the mercurous chromate thereby thrown down yields by ignition the anhydrous sesquioxide. The chromic acid might also be precipitated and estimated in the form of a baryta or lead salt.

Chromic acid may also be estimated by means of oxalic acid, which reduces it to sesquioxide, being itself converted into carbonic acid. The quantity of carbonic acid evolved determines the quantity of chromic acid present, 3 eq. CO_2 corresponding to 1 eq. CrO_3, as shown by the equation:

$$2CrO_3 + 3C_2O_3 = Cr_2O_3 + 6CO_2.$$

The mode of proceeding is the same as that adopted for the valuation of black oxide of manganese (p. 438). If the object be merely to determine the quantity of chromium present, any salt of oxalic acid may be used; but if the alkalies are also to be estimated in the remaining liquid, the ammonia or baryta salt must be used.

Chromic oxide, in the state of neutral or acid solution, is easily separated from the *alkalies* or *alkaline earths*, by precipitation with ammonia, care being taken in the latter case to protect the liquid and precipitate from the air. The same method, with addition of sal-ammoniac, serves to separate chromic oxide from *magnesia*. The separation from the alkaline earths and from magnesia may also be effected by precipitating the whole with an alkaline carbonate, and igniting the precipitate with a mixture of carbonate of soda and nitre. The chromium is then converted into chromate of soda, which may be dissolved out, and the solution, after neutralization with nitric or acetic acid, treated with mercurous nitrate as above.

From *alumina* and *glucina*, chromic oxide may be separated by treating the solution with excess of potash, and boiling the liquid to precipitate the chromic oxide. The separation is, however, more completely effected by fusing with nitre and carbonate of soda, treating the fused mass with water, adding an excess of nitric acid to dissolve anything that may be insoluble in water, and precipitating the alumina or glucina by ammonia.

Another method of converting chromic oxide into chromic acid, and thereby effecting its separation from the abovementioned oxides, is to treat the mixture with excess of potash, and heat the solution gently with bioxide of lead. The whole of the chromium is then converted into chromic acid, and remains dissolved as chromate of lead in the alkaline liquid; and on filtering from the excess of bioxide of lead, and any other insoluble matter that may be present, and supersaturating the filtrate with acetic acid, the chromate of lead is precipitated (Chancel).*

Chromic acid may be separated from the alkalies in neutral solutions by precipitation with mercurous nitrate; also by reducing it to chromic oxide with hydrochloric acid and alcohol, and precipitating by ammonia. From the *earths* it may also be separated by this latter method, or, again, by fusing with carbonate of soda, dissolving out with water, &c.

From *manganese*, *iron* (in the state of protoxide), *cobalt*, *nickel*, and *zinc*, chromium in the state of sesquioxide may be separated by agitation with carbonate of baryta, which precipitates the chromic oxide, leaving the protoxides in solution. The precipitate is then treated with dilute sulphuric acid, which dissolves the chromic oxide and leaves the baryta, and the filtrate treated with ammonia to precipitate the chromic oxide. Chromium may also be separated from all these metals, except manganese, by fusion with nitre and carbonate of soda, or with the carbonate alone if it is already in the form of chromic acid; or again, the separation may be effected by means of potash and bioxide of lead, according to Chancel's method above described.

From *cadmium*, *copper*, *lead*, and *tin*, chromium is easily separated by hydrosulphuric acid.

When sesquioxide of chromium and chromic acid occur together in a solution, the chromic acid may be precipitated by mercurous nitrate, the solution being first completely neutralized, and the sesquioxide precipitated from the filtrate by ammonia, which at the same time throws down a mercury-compound, to be afterwards separated from the chromic acid by ignition.

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* Compt. rend. xliii., 927.

SECTION IV.

VANADIUM.

Eq. 68·55 *or* 856·9; V.

Vanadium, so named from *Vanadis*, a Scandinavian deity, was discovered by Sefstrœm in 1830, in the iron prepared from the iron ore of Taberg, in Sweden, and procured afterwards in larger quantity from the slag of that ore. It was found afterwards by Mr. Johnston, in a new mineral discovered by him, the vanadiate of lead, from Wanlockhead. It is one of the rarest of the elements. The metal itself has considerable resemblance in properties to chromium. It combines with oxygen in three proportions, forming the protoxide of vanadium, VO, bioxide, VO_2, and vanadic acid, VO_3.

Protoxide of vanadium, VO, 76·55 *or* 95·69, is produced by the action of charcoal or hydrogen upon vanadic acid. It is a black powder of semi-metallic lustre, and when made coherent by pressure, conducts electricity like a metal. It does not combine with acids, and exhibits none of the characters of an alkaline base. It is readily oxidized when heated in the open air, and passes into the following compound.

Bioxide of vanadium, *Vanadic oxide*, VO_2, 84·55 *or* 1056·9, is produced by the action of hydrosulphuric acid and other deoxidating substances upon vanadic acid. When pure, it is a black pulverulent substance, quite free from any acid or alkaline reaction. It dissolves in acids, and forms salts, most of which are of a blue colour. Vanadic salts form, with the *hydrates* and *monocarbonates* of the *fixed alkalies*, a greyish-white precipitate of hydrated vanadic oxide, which dissolves in a moderate excess of the reagent, but is precipitated by a large excess in the form of a vanadite of the alkali. *Ammonia* in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia. *Ferrocyanide of potassium* forms a yellow precipitate, which turns green on exposure to the air. *Hydrosulphuric acid* produces no precipitate. *Sulphide of ammonium* forms a black-brown precipitate, soluble in excess. *Tincture of galls* forms a finely-divided black precipitate, which gives to the liquid the appearance of ink.

Bioxide of vanadium is also capable of acting as an acid, and forms compounds with alkaline bases, some of which are crystallizable. It is hence called *vanadous acid*, and its salts *vanadites*. These salts in the dry state are brown or black; they are all insoluble in water, excepting those of the alkalies. The solutions of the alkaline vanadites are brown, but when treated with hydrosulphuric acid, they acquire a splendid red-purple colour, arising from the formation of a sulphur-salt. Acids colour them blue, by forming a double salt of vanadic oxide and the alkali. Tincture of galls colour them blackish-blue. The insoluble vanadites, when moistened or covered with water, become green, and are converted into salts of vanadic acid.

Vanadic acid, VO_3; 92·55 *or* 1156·9.—It is in this state that vanadium occurs in the slag of the iron-ore of Taberg, and in the vanadiate of lead. It is obtained by dissolving the latter mineral in nitric acid, and precipitating the lead and arsenic, with which the vanadium is accompanied, by hydrosulphuric acid. A blue solution of bioxide of vanadium remains, which becomes vanadic acid when evaporated to dryness. Vanadic acid fuses, but retains its oxygen at a strong red heat. It is very sparingly soluble, water taking up only 1·100th of its weight of this compound, thereby acquiring a yellow colour and an acid reaction. It acts the part of a base to stronger acids. An interesting double phosphate of silica and vanadic acid was observed in crystalline scales, of which the formula is

$2SiO_3.PO_5 + 2VO_3.PO_5 + 6HO$. Vanadic acid forms, with bases, neutral and acid salts, the first of which admit of an isomeric modification, being both white and yellow, while the acid salts are of a fine orange-red. Vanadic and chromic acids are the only acids of which the solution is red, while they are distinguished from each other by the vanadic acid becoming blue, and the chromic acid green, when they are deoxidized. All the vanadiates are, more or less, soluble in water; some of them, however, as the baryta and lead salts, are very sparingly soluble. The vanadiates of the alkalies are sparingly soluble in cold water, especially if it contains a free alkali or another alkaline salt; *e. g.*, vanadiate of ammonia is nearly insoluble in water containing sal-ammoniac; hence on treating a solution of vanadiate of potash with excess of sal-ammoniac, a precipitate of vanadiate of ammonia is produced. The aqueous solutions of the vanadiates are coloured red by the stronger acids, but the mixture often becomes colourless again after a while. They give orange-red precipitates with the salts of *teroxide of antimony*, *protoxide of lead*, *protoxide of copper*, and *protoxide of mercury*. *Hydrosulphuric acid* produces in neutral solutions of the vanadiates a mixed precipitate of sulphur and hydrated vanadic oxide; in acid solutions, it merely throws down sulphur and reduces the vanadic acid to vanadic oxide. *Sulphide of ammonium* imparts to solutions of the vanadiates a brown-red colour, and, on adding an acid to the solution, a light brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur; the liquid at the same time generally acquires a blue colour.

All compounds of vanadium heated with *borax* or *phosphorus salt* in the outer blowpipe flame, produce a clear bead, which is colourless if the quantity of vanadium be small, yellow if it be large; in the inner flame, the bead acquires a beautiful green colour.

Sulphides and chlorides of vanadium, corresponding with the bioxide and vanadic acid, have likewise been formed.*

ESTIMATION OF VANADIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Vanadium, in the state of vanadic oxide or vanadic acid, is estimated by reducing it to the state of protoxide by ignition in a stream of hydrogen; 100 parts of the protoxide contain 90·54 of the metal.

In solutions of vanadous salts, the vanadium is precipitated by mixing the solution with excess of mercuric chloride (corrosive sublimate), and then with ammonia. The precipitate, consisting of mercuric vanadiate, and amido-chloride of mercury, is ignited, whereupon vanadic acid remains mixed only with a small quantity of mercuric oxide, from which it is separated by solution in carbonate of ammonia.

When vanadic acid is dissolved in a liquid, it may be obtained by evaporating the liquid, and if volatile acids or ammonia are also present, by igniting the residue.

Vanadic acid may be separated from many acids and other substances, by causing it to unite with ammonia, expelling the excess of ammonia by evaporation, and then adding a saturated solution of sal-ammoniac, in which vanadiate of ammonia is insoluble. The precipitate is then washed on a filter, first with solution of sal-ammoniac, then with alcohol, and the ammonia driven of by ignition. This method serves to separate vanadic acid from the fixed alkalies.

Vanadium may be separated from many of the preceding metals by the solubility of its sulphide in sulphide of ammonium; and from others, which are precipitated from their acid solutions by hydrosulphuric acid, by acidulating the liquid, and passing hydrosulphuric acid gas through it; the vanadium then remains dissolved in the form of vanadic oxide.

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* Berzelius, Ann. Ch. Phys. [2.] xlvii. 337.

From *lead*, *baryta*, and *strontia*, vanadic acid may be separated by fusion with bisulphate of potash; on treating the fused mass with water, sulphate of lead, baryta, or strontia remains, while vanadiate of potash is dissolved. Sulphuric acid cannot be used to effect this separation, because the precipitated sulphate always carries down with it a portion of the vanadium.

SECTION V.

TUNGSTEN.

Syn. WOLFRAM. *Eq.* 94·64, *or* 1183; W.

This element exists in the form of tungstic acid in several minerals, the most important of which are the native *tungstate of lime*, $CaO.WO_3$, and *wolfram*, or the tungstate of manganese and iron, $MnO.WO_3 + 3(FeO.WO_3)$. Its name tungsten means in Swedish, *heavy stone*, and is expressive of the great density of its compounds.

Tungstic acid parts with oxygen easily, and may be reduced in a glass tube, by means of dry hydrogen gas, at a red heat. The metal is thus obtained in the state of a dense, dark grey powder, which it is necessary to expose to a very violent heat to fuse into globules, for tungsten is even less fusible than manganese. The metal, when fused, has the colour and lustre of iron, and is not altered in air: it is one of the densest of the metals, its specific gravity being from 17·22 to 17·6. By passing the vapour of chloride or oxychloride of tungsten mixed with hydrogen, through a red-hot glass tube, the metal is obtained in the form of a dense specular film of steel-grey colour, and sp. gr. 16·54 (Wöhler). When heated to redness in the pulverulent form, it takes fire, burns, and is converted into tungstic acid. Tungsten forms two compounds with oxygen, viz., tungstic oxide, WO_2, and tungstic acid, WO_3.

Tungstic oxide, WO_2, 110·64 or 1383.—This oxide is obtained as a brown powder when tungstic acid is reduced by hydrogen at a temperature not exceeding low redness. Tungstic acid may also be deprived of oxygen in the humid way, by pouring diluted hydrochloric acid over it, and placing zinc in the liquor; the tungstic acid then gradually changes into tungstic oxide, in the form of brilliant crystalline plates of a copper-red colour. No saline compounds of this oxide with acids are known. When digested in a strong solution of hydrate of potash, it dissolves, with disengagement of hydrogen gas and formation of tungstate of potash.

A compound of tungstic oxide and soda, $NaO.2WO_2$, of a very singular nature, was discovered by Wöhler. It is obtained by adding to fused tungstate of soda as much tungstic acid as it will take up, and exposing the mass at a red heat to hydrogen gas. After dissolving out the neutral undecomposed tungstate by water, the new compound remains in golden yellow scales and regular cubes, possessing the metallic lustre of, and a striking resemblance to gold. This compound is not decomposed by aqua regia, sulphuric or nitric acid, or by alkaline solutions, but yields to hydrofluoric acid. It cannot be prepared by uniting soda directly with tungstic oxide.

Tungstic acid, WO_3; 118·64 or 1483, is most conveniently obtained by decomposing the native tungstate of lime, finely pulverized, by hydrochloric acid; chloride of calcium is dissolved, and tungstic acid precipitates. It is also obtained from wolfram by digesting that mineral in nitro-hydrochloric acid, which dissolves the oxides of iron and manganese, and leaves the tungstic acid in the form of a yellow powder—or by fusing the mineral with four times its weight of nitre; treating the fused mass with water to dissolve out the tungstate of potash thereby produced; adding chloride of calcium to the filtrate to throw down the tungstic acid as tungstate of lime; and decomposing the washed lime-salt with nitric acid. Dissolved in ammonia and reprecipitated by acids, tungstic acid always forms a compound with the acid employed. It may be obtained in the separate state by heating the tungstate of ammonia to redness. It is an orange-yellow powder, which becomes dull green when strongly heated. Its density is 6·12. It is quite insoluble in water and in acids, but dissolves in alkaline solutions.

Tungstic acid forms both neutral and acid salts with the alkalies. Neutral *tungstate of potash*, $KO.WO_3$, is a very soluble salt, which may be obtained in small crystals by evaporating its solution. When a little acid is added to the solution, an acid salt precipitates, which is very slightly soluble in water. The neutral *tungstate of soda* is also very soluble, but may be obtained in good crystals, which contain a large quantity of water of crystallization. The acid tungstate of soda, $NaO.2WO_3$, is very crystallizable, and soluble in eight parts of water. A combination of tungstic acid with tungstic oxide, $WO_2.WO_3$, is obtained as a fine blue powder when tungstate of ammonia is heated to redness in a retort, and is also produced under other circumstances. Malaguti is disposed to consider this compound as a distinct acid of tungsten, W_2O_5.*

All the salts of tungstic acid have a very high specific gravity. The alkaline and earthy tungstates are colourless. The only soluble tungstates are those of the alkalies and magnesia. Solutions of the alkaline tungstates give, with hydrochloric, nitric, sulphuric, and phosphoric acid, white precipitates consisting of compounds of tungstic acid with the other acid. The precipitate formed by phosphoric acid dissolves in excess of that reagent; the precipitates formed by the other three acids turn yellow on boiling. A solution of an alkaline tungstate supersaturated with sulphuric, hydrochloric, phosphoric, oxalic or acetic acid, yields, on the introduction of a piece of zinc, a beautiful blue colour arising from the formation of blue oxide of tungsten; this effect is not produced with nitric, tartaric, or citric acid. Solutions of alkaline tungstates form with lime-water and with salts of baryta, lime, zinc, lead, mercury, and silver, white precipitates consisting of tungstates of those bases. A soluble tungstate mixed with sulphide of ammonium and then with an acid in excess, yields a light brown precipitate of sulphide of tungsten, soluble in sulphide of ammonium.

With borax and phosphorus-salt in the outer blow-pipe flame, tungstic acid forms a colourless bead; in the inner flame it forms with borax, a yellow glass, if the quantity of tungsten present be somewhat considerable, but colourless with a smaller quantity. With phosphorus-salt in the inner flame it forms a glass of a pure blue colour, unless iron is also present, in which case the colour is blood-red; the addition of tin, however, renders it blue.

The above mentioned characters of tungstic acid, though general, are not invariable. Tungstic acid appears to be susceptible of certain modifications analogous to those of phosphoric acid, and depending upon the proportions in which it unites with water and other bases. In some of these modifications it is much more soluble than in others, and is not precipitated by nitric or hydrochloric acid.

Laurent distinguished five or six classes of tungstates, viz.,

1. *Ordinary tungstates*, WO_3MO, with or without water (M denoting a metal or hydrogen). To this class belong the neutral potash, soda, and baryta-salts, and most of the insoluble salts of tungstic acid. No acid salts of this class appear to exist. The solution of an ordinary tungstate dropped into excess of dilute nitric acid produces a gelatinous precipitate. The hydrated tungstic acid obtained by the action of aqua regia on wolfram belongs to this variety, its formula being $WO_3.HO$. 2. *Paratungstates*, $W_4O_{12}.2MO$, with or without water. To this class belong the salts commonly called bitungstates of potash, soda, ammonia, baryta, &c. They all, excepting the soda-salt, dissolve but sparingly in water. The solutions give no precipitate on the addition of very small quantities of nitric acid.

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* Ann. Ch. Phys. [2], lx. 271.

or of very weak hydrochloric acid. They give precipitates with the ammoniacal solutions of nitrate of magnesia, zinc, and silver, which the ordinary tungstates do not. 3. *Metatungstates*, $W_3O_9.MO$, with or without water. The ammonia-salt of this variety is formed by boiling a solution of the paratungstate for several hours; the solution filtered when cold and then evaporated to a syrup, yields very soluble octohedrons. The solution is not precipitated by concentrated hydrochloric acid.—4. *Isotungstates*, $W_2O_6.MO$, with or without water. The ammonia-salt is formed by boiling metatungstate of ammonia with excess of ammonia; it is but slightly soluble in water. The acid, which may be separated from it by means of another acid, is principally characterized by reproducing the isotungstate when treated with ammonia. 5. *Polytungstates*, $W_6O_{18}.3MO$. When the yellow acid obtained from wolfram is treated with ammonia, and the solution slowly evaporated, paratungstate of ammonia is first deposited and afterwards the isotungstate. The mother-liquor separates into two layers, one of which is brown and syrupy, and changes on drying to an easily soluble crystalline mass, probably a double salt of ammonia and iron. Boiled with strong nitric acid, it yields a precipitate which is not gelatinous, and does not turn yellow when boiled. Polytungstic acid is further characterized by forming with ammonia a very soluble salt, which becomes gummy on evaporation. 6. Laurent also, mentioned another class of tungstates, viz., *Homotungstates*, containing $W_5O_{15}.MO$. According to Margueritte* also there exist acid tungstates containing 3, 4, 5 and 6 eq. of acid to 1 eq. of base.

The composition of the tungstates has also been recently examined by W. Lotz,† whose results differ in many points from the preceding. According to Lotz, crude tungstic acid, obtained from wolfram by the action of hydrochloric and a small quantity of nitric acid, yields by digestion with ammonia and evaporation at a very gentle heat, yellow needles of an ammonia-salt, containing $3NH_4O.7WO_3+6HO$, or $2(NH_4O.\ 2WO_3)+NH_4O.\ 3WO_3+6HO$. By mixing warm concentrated solutions of 1 eq. of monotungstate of soda, and rather more than 1 eq. chloride of ammonium, a double salt is obtained, composed of $(2NH_4O.WO_3)+NaO.WO_3+3HO$; and by adding 1 eq. metatungstate of soda to a boiling solution of 2 eq. chloride of ammonium, another double salt is formed containing $3NaO.7WO_3+4(3NH_4O.7WO_3)+14HO$. The needle-shaped ammonia-salt mixed with solutions of the neutral salts of barium, strontium, manganese, nickel, and lead, yields precipitates of the general formula, $3MO.7WO_3$. With alumina a white curdy precipitate is formed containing $Al_2O_3.7WO_3+9HO$. Sesquioxide of chromium forms a salt of a similar constitution. With magnesia, a sparingly soluble crystalline double salt is formed, containing $2(MgO.2WO_3)+NH_4O.3WO_3+10HO$; a similar double salt with zinc. Cadmium also forms a double salt containing $3NH_4O.7WO_3+4(3CdO.7W_3O)+35HO$. To the octohedral tungstate of ammonia, which was regarded by Margueritte as $NH_4O.3WO_3+5HO$, and by Laurent as a metastungstate containing $(NH_4)_{\frac{5}{6}}H_{\frac{1}{6}}W_3O_{10}+5HO$, or $\left.\begin{matrix}5NH_4O\\HO\end{matrix}\right\}18WO_3+30HO$. Lotz assigns the formula, $2(NH_4O.4WO_3)+15$eq. The solution of this salt is not precipitated by nitric or hydrochloric acid at ordinary temperatures, but after continued boiling yields a yellow precipitate; but if it be previously mixed with potash, the addition of an acid produces an immediate white precipitate, which turns yellow on boiling; the needle-shaped salt gives an immediate precipitate with acids, without previous addition of alkali. The octohedral salt differs from the needle-shaped salt also, in not forming precipitates with solutions of the earths and other metallic oxides, except when previously mixed with ammonia, by which, indeed, it is converted into the salt, $3NH_4O.7WO_3$.

Sulphides of tungsten.—The bisulphide is prepared by mixing one part of

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* Ann. Ch. Phys. [3], xvii. 475.

† Ann. Ch. Pharm. xci. 49.

tungsten with six parts of cinnabar, and exposing the mixture, covered with charcoal, in a crucible, to a white heat; or, according to Roche, by fusing bitungstate of potash with an equal weight of sulphur, and washing the fused mass with water. The tersulphide is formed by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid. It is of a liver-brown colour, and becomes black on drying. The tersulphide of tungsten has a certain degree of solubility in water containing no saline matter, and is a strong sulphur-acid. The salt $KS.WS_3$ forms pale red crystals. Two parts of this sulphur-salt dissolved in water with one part of nitre, give large and beautiful ruby-red crystals of a double salt, $KS.WS_3 + KO.NO_5$.

Phosphides of tungsten.—Phosphorus and tungsten combine directly, but without emission of light and heat, when finely pounded metallic tungsten contained in a glass tube is heated to redness in phosphorus vapour. The resulting compound is a dull, dark grey powder, very difficult to oxidize, and containing W_3P_2. Another compound, W_4P, is obtained in magnificent crystalline groups, having exactly the appearance of natural geodes, by reducing a mixture of 2 eq. phosphoric and 1 eq. tungstic acids at a very high temperature in a crucible lined with charcoal. The crystals are six-sided prisms, sometimes an inch long, of a steel-grey colour, and strong lustre; their specific gravity is 5·207. This compound is a perfect conductor of electricity; undergoes no change when heated to the melting point of manganese in a close vessel, and remains nearly unaltered when heated to redness in the air; but burns with great splendour on charcoal in a stream of oxygen, or on fused chlorate of potash; it is not attacked by any acid, not even by aqua-regia (Wöhler).*

Bichloride of tungsten, WCl_2, is formed when metallic tungsten is heated in chlorine gas. It condenses in dark red needles, which are very fusible and volatile. This chloride is decomposed by water, and tungstic oxide with hydrochloric acid formed.

Terchloride of tungsten, WCl_3, is produced at the same time as the last compound, and also when the sulphide of tungsten is heated in chlorine gas. It forms a sublimate of beautiful red crystals, which are resolved by water into tungstic and hydrochloric acids. A *chlorotungstic acid*, or double compound of terchloride of tungsten and tungstic acid, WO_2Cl, or $WCl_3.2WO_3$, is prepared by heating tungstic oxide in chlorine gas. It condenses in yellow crystalline scales: when suddenly heated, it is resolved into tungstic acid, bichloride of tungsten, and chlorine. Another compound is known, containing $2WCl_3.WO_3$ (Bonnet).

According to A. Riche,† the terchloride of tungsten is the only product obtained when tungsten is heated in pure dry chlorine gas: it crystallizes in needles, not of a red but of a steel-grey colour. The bichloride is formed in small quantity, as a blackish-brown mass, by heating the terchloride in dry hydrogen; and the red oxychloride, WCl_2O, by passing chlorine gas over a mixture of tungstic acid and charcoal, and distilling the product in an atmosphere of hydrogen.

ESTIMATION OF TUNGSTEN, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Tungsten is always estimated in the form of tungstic acid. When this acid exists in a solution not containing any other fixed substance, it is sufficient to evaporate to dryness and ignite the residue. The tungstic acid is then obtained in a state of purity, and contains 79·76 per cent. of the metal. Tungstic oxide is easily converted into tungstic acid by fusion with carbonate of soda.

The best method of separating tungstic acid from the *fixed alkalies* is to treat the solution, after exact neutralization with nitric acid, with a solution of mercurous nitrate. Mercurous tungstate is then precipitated, and the mercury may be expelled from the dried precipitate by careful ignition in a good draught.

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* Chem. Soc. Qu. J. v. 94.

† Compt. rend. xlii. 203.

The separation of tungstic acid from the *earths* may be effected by decomposing the compound with nitric acid, and treating the decomposed mass with carbonate of ammonia, which dissolves the tungstic acid.

Tungstic acid may be readily separated from many metallic oxides, such as the oxides of *iron*, *manganese*, *nickel*, *cobalt*, *lead*, &c., by fusing the whole with carbonate of soda, and digesting the fused mass with water, which dissolves the tungstic acid and leaves the oxides undissolved.

From *titanic acid*, tungstic acid is separated by ammonia, which dissolves only the latter.

The best mode of separating tungstic acid from *chromic acid*, is to treat the concentrated solution with excess of hydrochloric acid, which precipitates the greater part of the tungstic acid; then boil with alcohol to reduce the chromic acid to chromic oxide; and dissolve the tungstic acid by ammonia.

SECTION VI.

MOLYBDENUM.

Eq. 47·88 *or* 598·5; Mo.

This metal is closely allied to tungsten. Its native sulphide was first distinguished from plumbago by Scheele, in 1778; and a few years afterwards, molybdic acid, which he had formed, was reduced, and molybdenum obtained from it, by another Swedish chemist, Hjelm. The name molybdenum is derived from the Greek term for plumbago.

The oxides of molybdenum are easily reduced, when exposed to a strong heat in a crucible lined with charcoal, but the metal itself is very refractory. Bucholz, who obtained it in rounded buttons, found it to be a white metal, of density between 8·615 and 8·636. It may be reduced from its chlorides by hydrogen, like tungsten (p. 177), and then forms a light steel-grey specular deposit, adhering to the glass (Wöhler). It is not acted upon by hydrochloric, hydrofluoric, or diluted sulphuric acid; but is dissolved by concentrated sulphuric acid, by nitric acid, and by aqua-regia. Hydrate of potash does not dissolve this metal in the humid way. Molybdenum combines in three proportions with oxygen, forming molybdous oxide, MoO, molybdic oxide, MoO_2, and molybdic acid, MoO_3.

Molybdous oxide, MoO, 55·88 *or* 698·5.—This oxide is obtained by adding to the concentrated solution of any molybdate, so much hydrochloric acid as to redissolve the molybdic acid which is at first thrown down, and placing zinc in the liquid; this becomes first blue, then reddish-brown, and finally black, and contains the chloride of zinc and protochloride of molybdenum. To separate the oxide of molybdenum from the oxide of zinc, ammonia is added to the liquid in quantity no more than sufficient to precipitate the former, while the latter remains in solution. The molybdous oxide carries down with it a portion of oxide of zinc, from which it may be freed by washing with ammonia: it is thus obtained as a hydrate of a black colour. The hydrate of molybdous oxide dissolves with difficulty in acids, forming solutions which are almost black and opaque, and which do not yield crystallizable salts. These solutions yield with the *alkalies* and their *carbonates* a brownish-black precipitate of the hydrated oxide, insoluble in the caustic alkalies, slightly soluble in the neutral carbonates, but readily soluble in bicarbonate of potash or carbonate of ammonia. *Hydrosulphuric acid* throws down a brown-black precipitate, and *sulphide of ammonium* a yellowish-brown precipitate of sulphide of molybdenum, easily soluble in sulphide of ammonium. *Ferrocyanide* or *ferricyanide* of potassium forms a dark-brown precipitate, insoluble in excess. *Phosphate of soda* forms a brownish-white precipitate. Molybdous oxide resists, after ignition, the action of all acids.

Molybdic oxide, MoO_2; 63·88 *or* 798·5.—This oxide may be obtained by igniting molybdate of ammonia in a covered crucible, but mixed with a little molybdic acid. It is better procured by igniting rapidly, in a covered crucible, a mixture of anhydrous molybdate of soda (which may contain an excess of soda) with sal-ammoniac. Water poured upon the fused mass dissolves common salt, and leaves a brown powder, almost black. But molybdic oxide prepared in this way is insoluble in acids. The hydrated oxide may be obtained in various ways, one of which consists in digesting molybdic acid with hydrochloric acid and copper, till all the molybdic acid is dissolved. From the solution, which is of a deep-red colour, molybdic oxide is precipitated, in appearance exactly similar to the hydrated sesquioxide of iron, by ammonia added in sufficient excess to retain all the oxide of copper in solution. The hydrate has a certain degree of solubility in pure water, and should, therefore, be washed with solution of sal-ammoniac, and lastly with alcohol. This hydrate reddens litmus paper, but possesses no other property of an acid. It is not dissolved by the hydrated alkalies, but is soluble in their carbonates, like several earths and metallic oxides. It dissolves in acids and forms salts, which are red when they contain water of crystallization, and black when anhydrous. The aqueous solutions of these salts have a reddish-brown colour, and a rough, somewhat acid and subsequently metallic taste. When heated in the air, they have a tendency to become blue by oxidation. With *zinc*, they first blacken, and then yield a black precipitate of hydrated molybdous oxide. Their behaviour with alkalies, hydrosulphuric acid, &c., is similar to that of the molybdous salts, excepting that the precipitates are lighter in colour. The oxalate of molybdic oxide may be obtained in crystals by spontaneous evaporation.

Molybdic acid, MoO_3; 71·88 *or* 898·5.—The native sulphide of molybdenum, in fine powder, is roasted in an open crucible, with constant stirring, at a heat not exceeding low redness, so long as sulphurous acid goes off. It leaves a dull yellow powder, which is impure molybdic acid. This is dissolved in ammonia, and the molybdate of ammonia purified by evaporation, during which some foreign matters are deposited, and crystallized. The crystallized salt, exposed to a moderate heat, so as to avoid fusion, gives off its ammonia, and leaves molybdic acid in a state of purity. The acid thus prepared is a white and light porous mass, which may be diffused in water, and divides into little crystalline scales of a silky lustre. It fuses at a red heat, and forms on cooling a straw-coloured crystalline mass, the density of which is 3·49. This acid forms no hydrate. It requires 570 times its weight of water to dissolve it. Before being ignited, it is soluble in acids, and forms a class of compounds, in which it appears to play the part of base, but of which not much is known. When boiled with bitartrate of potash, molybdic acid dissolves, even after being fused by heat.

When a solution of bichloride of molybdenum is poured into a saturated or nearly saturated solution of molybdate of ammonia, a blue precipitate falls, which is a *molybdate of molybdic oxide*, $MO_2.2MO_3$. This compound is likewise readily formed in a variety of other circumstances.

The salts of molybdic acid are colourless, when their base is not coloured. When they are treated with other acids, molybdic acid is precipitated, but dissolves in an excess of the acid. It forms both neutral and acid salts with the alkalies. These alkaline molybdates are the only ones that are easily soluble in water; of the rest, some dissolve sparingly, and others are completely insoluble. Solutions of the alkaline molybdates are coloured yellow by *hydrosulphuric acid* from formation of a sulphomolybdate of the alkali-metal (MS,MOS_3), and then yield with acids a brown precipitate of tersulphide of molybdenum. This is an extremely delicate test for molybdic acid. They form white precipitates with salts of the *earths*, and precipitates of various colours with salts of the heavy metals; *e. g* white with *lead* and *silver* salts; yellow with *ferric* salts; and yellowish-white with *mercurous* salts.—*Protochloride of tin* produces immediately a greenish blue precipitate, soluble in hydrochloric acid forming a green solution; which turns blue on the addition of a very small quantity of the tin-solution.—When *tribasic phosphoric acid*, or a liquid containing it, is added to the solution of molybdate of ammonia, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic acid combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The bibasic and monobasic phosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction. According to Seligsohn,* the yellow precipitate is a *phosphomolybdate of ammonia*, $2(3NH_4O.PO_5) + 15(HO.4MoO_3.)$ By digesting it in a dilute solution of acetate of potash or soda, crystalline double salts are formed, containing $2(3NH_4O.PO_5) + 15\left(\left.\begin{matrix}KO\\ \text{or } NaO\end{matrix}\right\}.4MoO_3\right)$. With acetate of baryta, a double salt is formed, containing $3NH_4O.PO_5 + 30(BaO.MoO_3)$; and similarly with acetate of lead.

Molybdic acid and other compounds of molybdenum form a colourless bead with *borax* and *phosphorus-salt* in the outer blowpipe flame. In the inner flame, they form a brown bead with borax and a green bead with phosphorus-salt.

Molybdates of potash. — The *monomolybdate*, $KO.MoO_3$, is obtained by agitating the termolybdate with an alcoholic solution of potash: it then separates as an oily mass, which, when dried over lime and sulphuric acid, crystallizes in four-sided prisms containing $2(KO.MoO_3) + HO$. It is also obtained by mixing a solution of molybdate of ammonia with excess of carbonate of potash, and evaporating to a syrup. Bimolybdate of potash does not appear to exist. When a solution of molybdic acid in carbonate of potash is mixed with strong nitric or hydrochloric acid till a slight permanent precipitate is produced, the liquid after a while yields crystals of a salt containing $4KO.9MoO_3 + 6HO$; and this salt is decomposed by water into monomolybdate, which dissolves readily, and termolybdate, which is sparingly soluble:

$$2(4KO.9MoO_3) = 3(KO.MoO_3) + 5(KO.3MoO_3).$$

The *termolybdate* dissolves easily in boiling water, and separates as a bulky white precipitate when the solution is quickly cooled; but by slow cooling it is obtained in needles, having a beautiful silky lustre and containing $KO.3MoO_3 + 3HO$. Nitric acid added in excess to a solution of molybdic acid in carbonate of potash throws down a white precipitate consisting sometimes of *quadromolybdate* and sometimes of *pentamolybdate* of potash, both anhydrous (Svanberg and Struve).†

Monomolybdate of soda, $NaO.MoO_3 + 2HO$, is obtained by fusing molybdic acid with an equivalent quantity of carbonate of soda. It is easily soluble in water, and crystallizes in small rhombohedrons, which melt easily and give off their water. The *bimolybdate*, $NaO.2MoO_3 + HO$, is obtained in a similar manner. It crystallizes in needles, and dissolves sparingly in cold, readily in boiling water. The *termolybdate* is obtained by adding nitric acid to a solution of molybdic acid in carbonate of soda, as a bulky white precipitate, more soluble than the corresponding potash-salt. The solution yields crystals containing $NaO.3MoO_3 + 7HO$. Nitric acid added in excess to a solution of molybdate of soda throws down nothing but molybdic acid (Svanberg and Struve).‡

Monomolybdate of ammonia, $NH_4O.MoO_3$, obtained by treating molybdic acid in excess with strong solution of ammonia in a closed vessel, then precipitating with alcohol, and drying over quicklime, forms microscopic four-sided prisms,

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* J. pr. Chem. lxvii. 474.

† Ann. Ch. Pharm. lxviii. 494.

‡ Ann. Ch. Pharm. lxviii. 404.

which are anhydrous. The *bimolybdate*, $NH_4O.2MoO_3$, is deposited as a white crystalline powder when a solution of molybdic acid in excess of ammonia is quickly evaporated. A solution of molybdic acid in ammonia, evaporated by heat to the crystallizing point, or left to evaporate in the air, deposits large transparent six-sided prisms, containing $NH_4O.2MoO_3 + NH_4O.3MoO_3 + 3HO$ (Svanberg and Struve).

Monomolybdate of baryta, $BaO.MoO_3$, is precipitated as a sparingly soluble crystalline powder, on adding chloride of barium to a solution of molybdic acid in excess of ammonia. Baryta-salts, containing $BaO.3MoO_3 + 3HO$ and $BaO.2MoO_3 + BaO_2 3MoO_3 + 6HO$, are obtained by precipitating the corresponding potash and ammonia-salts with chloride of barium. By decomposing monomolybdate of baryta with dilute nitric acid, an acid salt is formed containing $BaO.9MoO_3 + 4HO$; it crystallizes in small six-sided prisms, fusible and insoluble in water (Svanberg and Struve).

Monomolybdate of magnesia, $MgO.MoO_3 + 5HO$, is obtained in distinct crystals by boiling molybdic acid and *magnesia alba* with water, and evaporating the filtrate; it gives off 3 eq. water at 212° (Struve).*

Molybdate of manganous oxide, $MnO.MoO_3 + HO$, is obtained as a heavy white powder, by treating carbonate of manganese with termolybdate of potash or soda.

Protosulphate of iron added to a solution of molybdate of potash, reduces the molybdic acid to a lower state of oxidation; but if chlorine gas be passed through the solution at the same time, a bulky precipitate is formed, which, when dried in the air, forms a light yellow powder, consisting of *pentamolybdate of ferric oxide*, $Fe_2O_3.5MoO_3 + 16HO$.

By boiling the solution of termolybdate of potash or soda, or acid molybdate of ammonia, with hydrate of *alumina*, *manganic oxide*, *ferric oxide*, or *chromic oxide*, and evaporating to the crystallizing point, double salts are obtained. The composition of the double salts containing alumina, ferric oxide, or chromic oxide, with potash or oxide of ammonium, may be represented by that of the alumina and potash-salt, viz., $Al_2O_3.6MoO_3 + 3(KO.2MoO_3) + 20HO$. The *potassio-manganic* salt contains $Mn_2O_3.6MoO_3 + 5(KO.2MoO_3) + 12HO$. The *ammonio-manganic* salt is similarly constituted. The *sodio-chromic* salt contains $Cr_2O_3.6MoO_3 + 3(NaO.2MoO_3) + 21HO$ (Struve).

Acid molybdate of ammonia, added to a boiling solution of sulphate of copper, throws down a heavy green amorphous powder, consisting of *basic molybdate of copper*, $4CuO.3MoO_3 + 5HO$. By adding molybdate of ammonia in excess to a cold solution of sulphate of copper, a double salt is formed, consisting of $CuO.2MoO_3 + NH_4O.3MoO_3 + 9HO$. It is a white-blue crystalline powder, which gives off 4 eq. of water at 212° and 4 eq. more at 266° (Struve).

Molybdate of lead, $PbO.MoO_3$, is formed by precipitating nitrate of lead with termolybdate of potash. It is a heavy white powder, which melts only at a high temperature. It occurs finely crystallized as a mineral. Chromate of lead is dimorphous, and corresponds in the least usual of its forms with molybdate of lead: hence molybdenum is connected with the magnesian metals, and tungsten also with the same class, from the isomorphism of the tungstates and molybdates.

Sulphides of molybdenum.—The *bisulphide* is the ore from which the compounds of this metal are derived. It occurs in many parts of Sweden, and might be procured in quantity if any useful application of the metal were discovered. It is a lead-grey mineral, having the metallic lustre, composed of flexible laminæ, soft to the touch, and making a streak upon paper like plumbago. Nitric acid oxidates it easily, without dissolving it. Its density is from 4·138 to 4·569. A *tersulphide of molybdenum* is obtained in the same way as the corresponding compound of tungsten, and affords crystallizable sulphur-salts which are red. The

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* Ann. Ch. Pharm. xcvi., 266.

sulphomolybdate of potassium combines likewise with nitrate of potash. When a solution of the former salt is boiled with tersulphide of molybdenum in excess, the latter is converted into bisulphide of molybdenum, and a *quadrisulphide of molybdenum* dissolves in combination with the sulphide of potassium. The quadrisulphide may be precipitated by hydrochloric acid, and when dried is a cinnamon-brown powder.

Chlorides of molybdenum.—A *protochloride* is formed when molybdous oxide is dissolved in hydrochloric acid; the *bichloride* when molybdenum is heated dry in chlorine gas, as a dark-red gas which condenses in crystals, like those of iodine. It forms a crystallizable double salt with sal-ammoniac. *Chloromolybdic acid*, or a compound of terchloride of molybdenum and molybdic acid, MoO_2Cl, or $MoCl_3 + 2MoO_3$, is formed with (molybdic acid), when molybdic oxide is exposed to chlorine gas at a red heat. It sublimes below a red heat, and condenses in crystalline scales, which are white with a shade of yellow.

ESTIMATION OF MOLYBDENUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The determination of molybdic acid is more difficult than that of tungstic acid, on account of its partial volatility. The best mode of estimating it is to convert it into molybdic oxide by ignition in an atmosphere of hydrogen; the oxide which is perfectly fixed may then be weighed; it contains 74·95 per cent. of the metal. When molybdic acid exists in solution in ammonia or in other acids, the solution must be carefully evaporated to dryness, and the residue treated as above.

Molybdic acid is separated from most metallic oxides by its solubility in sulphide of ammonium. The filtered solution is then treated with an excess of very dilute nitric acid, to precipitate the tersulphide of molybdenum; the precipitate collected on a weighed filter, and its quantity determined; after which, a weighed quantity of it is ignited in an atmosphere of hydrogen, to convert it into the bisulphide, MoS_2, from the weight of which the amount of molybdenum is calculated.

Molybdic acid is separated from the *earths* by fusing with carbonate of soda, and digesting the fused mass in water, which dissolves molybdate of soda, and leaves the earth in the form of carbonate.

From the *fixed alkalies*, molybdic acid may be separated by precipitation with mercurous nitrate, and its quantity estimated from the weight of the precipitate.

SECTION VII

TELLURIUM.

Eq. 64·14 *or* 801·8; Te.

Tellurium is a metal of rare occurrence, and appeared at one time to be almost confined to certain gold mines in Transylvania; but it has been found lately in considerable abundance, at Schemnitz, in Hungary, combined with bismuth; and in the silver mine of Sadovinski in the Altai, united with silver and with lead. It was first described as a new metal by Klaproth, who gave it the name of tellurium, from *tellus*, the earth.

Tellurium is chiefly obtained from telluride of bismuth. The ore, after being freed from the matrix by pounding and washing, is mixed with an equal weight of carbonate of potash or soda, the mixture made up into a paste with olive oil, and heated in a well-closed crucible, carefully at first to prevent frothing, and afterwards to a full white heat. The fused mass is then digested in water; which leaves the bismuth and the excess of charcoal undissolved, and dissolves the tellurium in the form of telluride of potassium or sodium, which imparts a port-wine colour to the liquid. The solution deposits metallic tellurium when exposed to the air, or more quickly when air is blown through it; and the precipitated metal is purified by washing with acidulated water, and subsequent distillation in an atmosphere of hydrogen (Berzelius). The metal is also obtained from the ore called *foliated tellurium*, which contains 13 per cent of tellurium, and 63 per cent. of lead, together with copper, gold, antimony, and sulphur. The finely pounded mineral is freed from the sulphide of lead and antimony by repeated boiling with strong hydrochloric acid and washing with water; the residual telluride of gold treated with strong nitric acid; the tellurium-solution poured off from the gold and evaporated to dryness; the residue dissolved in hydrochloric acid; and the tellurium precipitated from the solution by sulphurous acid (Berthier).*

In a state of purity, tellurium is silver-white and very brilliant. It is very crystallizable, assuming a rhombohedral form, in which it is isomorphous with arsenic and antimony. It is brittle for a metal, and an indifferent conductor of heat and electricity. Its density is from 6·2324 to 6·2578, according to Berzelius. Tellurium is about as fusible as antimony, and may be distilled at a high temperature. It burns in air, at a high temperature, with a lively blue flame, green at the borders, and diffuses a dense white smoke, which generally has the odour of decaying horse-radish, from the presence of a little selenium. Tellurium belongs to the sulphur-class of elements. Like selenium and sulphur, it dissolves to a small extent in concentrated sulphuric acid, and communicates to it a fine purple-red colour. In this solution, the metal is not oxidated, for it is precipitated again, in the metallic state, by water. This metal has also considerable analogy with antimony, and may probably connect together the sulphur and phosphorus families. Tellurium combines in two proportions with oxygen, forming tellurous acid, TeO_2, and telluric acid, TeO_3.

Tellurous acid, TeO_2; 80·14 *or* 1001·8. — This acid differs remarkably in properties according as it is anhydrous or hydrated.† Hydrated tellurous acid is obtained by precipitating bichloride of tellurium with cold water; or by fusing anhydrous tellurous acid with an equal weight of carbonate of potash, as long as carbonic acid is disengaged, dissolving the tellurite of potash in water, and adding nitric acid to it till the liquor distinctly reddens litmus paper. A white and bulky precipitate is produced, which is washed with ice-cold water, and afterwards dried without artificial heat. Tellurium likewise dissolves with violence in pure nitric acid of density 1·25, and if after the first five minutes, the clear liquid be poured into water, tellurous acid is precipitated in white flocks. But if not immediately precipitated, the nitric acid solution undergoes a change.

The hydrated acid obtained by these processes forms a light, white, earthy mass, of a bitter and metallic taste. It instantly reddens litmus paper, and while still moist, dissolves to a sensible extent in water. It is very soluble in acids, and the solutions are not subject to change, except that which is formed by nitric acid. Ammonia and the alkaline carbonates also dissolve hydrated tellurous acid with facility, the latter becoming bicarbonates.

Anhydrous tellurous acid. — When the solution of tellurous acid in water is heated to 140°, it deposits the anhydrous acid in grains, and loses its acid reaction. The same change occurs when an attempt is made to dry the hydrated tellurous acid by heat: it parts with combined water, and becomes granular. The solution of tellurous acid in nitric acid changes spontaneously in a few hours, and

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* For further details respecting the extraction of tellurium, vide Berzelius, Traité de Chimie, i. 344; and the translation of Gmelin's Handbook, iv. 393. Wöhler states, in a note to his paper on telluride of ethyl (Ann. Ch. Pharm. lxxxiv. 70), that tellurium may be obtained in considerable quantities from the residues of the Transylvanian gold-extraction, which have hitherto been thrown away as worthless.

† Berzelius regarded the hydrated and anhydrous acids as containing different modifications of the same compound, and distinguished them as α-tellurous and β-tellurous acid.

in a quarter of an hour when heat is applied to it, and allows the anhydrous acid to precipitate. When the deposition of the acid is slow, it forms a crystalline mass of fine grains, among which octohedral crystals may be perceived by the microscope. The acid is then anhydrous. In this state it does not redden litmus, or not till after a time. It is but very slightly soluble in water, and the solution has no acid reaction. At a low red heat, it fuses into a clear transparent liquid of a deep yellow colour, which on cooling becomes a white and highly crystalline mass, easily detached from a crucible. Tellurous acid is volatile, although less so than the metal itself.

The solutions of hydrated tellurous acid in the stronger acids yield a black precipitate of metallic tellurium, when treated with powerful deoxidizing agents, such as zinc, phosphorus, protochloride of tin, sulphurous acid, and the alkaline bisulphates. Hydrosulphuric acid and sulphide of ammonium throw down black-brown sulphide of tellurium, easily soluble in excess of sulphide of ammonium.

The *tellurites*, or compounds of tellurous acid with salifiable bases, contain 1 atom of base united with 1, 2, or 4 atoms of acid. They are fusible, and generally solidify in the crystalline form on cooling; the quadrotellurites, however, form a glass. Tellurites are colourless unless they contain a coloured base; those which are soluble have a metallic taste. Most of them, when heated to redness with charcoal, yield metallic tellurium, sometimes with slight detonation; and the reduced metal volatilizes readily, being at the same time reoxidized and forming a white deposit on the charcoal; it likewise imparts a green colour to the flame; the tellurites, when ignited with potassium, or with charcoal and carbonate of potash, yield telluride of potassium which dissolves in water, forming a port-wine coloured solution; with the zinc and silver-salts, however, and a few others, this reduction does not take place. The tellurites of ammonia, potash and soda are easily soluble in water; those of baryta, strontia, and lime are sparingly soluble; the rest, insoluble. An aqueous solution of a tellurite is decomposed by the carbonic acid of the air. Nearly all tellurites dissolve in strong hydrochloric acid without evolving chlorine when heated; the solution exhibits the above-mentioned characters of a solution of tellurous acid in the stronger acids, except in so far as it may be interfered with by the presence of another base. The solution when diluted in water yields a white precipitate of tellurous acid, provided the excess of hydrochloric acid present is not too great.

Monotellurite of potash, $KO.TeO_2$, is obtained by heating 1 eq. tellurous acid with eq. of carbonate of potash. The fused mass on cooling forms crystals of large size. The salt dissolves slowly in cold, more quickly in warm water. *Bitellurite of potash*, $KO.Te_2O_4$, is obtained by fusing two atoms of tellurous acid with one atom of carbonate of potash. It appears to be capable of existing in a hot solution, and of crystallizing in certain circumstances; but it is decomposed by cold water, which resolves it into the neutral salt, which dissolves, and a *quadritellurite of potash*, $KO.Te_4O_8 + 4HO$. The latter salt cannot be redissolved in water, without decomposition. In losing its water when heated, it swells up like borax.

Telluric acid, TeO_3; 88·14 *or* 1101·8. — This acid is obtained in combination with potash, by fusing tellurous acid with nitre. It may then be transferred to baryta, and the insoluble tellurate of baryta decomposed by sulphuric acid. The solution of telluric acid gives bulky, hexagonal, prismatic crystals. Its taste is not acid, but metallic, resembling that of nitrate of silver. Indeed, it appears to be but a feeble acid, reddening litmus but slightly, when the solution is diluted. The crystallized acid contains 3HO, of which it loses 2HO by efflorescence, a little above 212°. It then appears insoluble in cold water, but may be completely redissolved by long digestion, particularly with ebullition, and is not permanently altered.

Anhydrous telluric acid. — The crystals of hydrated telluric acid give off all their water at a heat below redness, and are converted into a mass of a fine orange-yellow colour, without changing their form. This yellow matter, which is distinguished, as *alpha-telluric acid* by Berzelius, is remarkable for its indifference to chemical reagents, being completely insoluble in cold or boiling water, in hot hydrochloric and nitric acids, and in potash-ley. At a high temperature, it is decomposed, evolving oxygen, and leaving tellurous acid white and pulverulent.

Telluric acid has but slight affinity for bases. The hydrated acid withdraws from alkaline carbonates, only so much alkali as to form a biacid salt. Telluric acid forms bibasic, sesquibasic, monobasic, biacid, and quadracid salts. The tellurates are colourless, unless they contain a coloured base. At a red heat, they give off oxygen and are converted into tellurites. Before the blowpipe, they behave like the tellurites; also with reducing agents, such as protochloride of tin, and sulphurous acid, excepting that the reduction does not take place so quickly, and in some cases requires the application of heat. Hydrosulphuric acid, added to the solution of a tellurate, produces no change at first; but if the liquid be placed in a stoppered bottle and left for a while in a warm place, a brown precipitate of sulphide of tellurium is formed. Tellurates dissolve in cold strong hydrochloric acid without decomposition. The solutions are not yellow, like those of the tellurites in hydrochloric acid, and may be diluted with water without becoming milky, even though the excess of hydrochloric acid be but small. But on boiling the solution, chlorine is evolved, and the liquid, if subsequently mixed with water, gives a precipitate of tellurous acid, provided the excess of hydrochloric acid is not too great.

Neutral *tellurate of potash* is $KO.TeO_3+5HO$; the *bitellurate of potash*, $KO.Te_2O_6+4HO$; the *quadritellurate of potash*, $KO.Te_4O_{12}+4HO$. All these salts may be obtained directly, in the humid way, by dissolving the proper proportions of hydrated acid and carbonate of potash together, in hot water. A portion of the combined water in the last two salts is unquestionably basic, but how much of it is so has not been determined. They cannot be made anhydrous by heat without being essentially altered in properties.

The neutral tellurate of potash undergoes no change in constitution under the influence of heat, resembling in that respect those tribasic phosphates of which the whole three atoms of base are fixed. The bitellurate of potash loses its water and becomes yellow at a temperature below redness, and is changed into a quadritellurate, which is insoluble both in water and in dilute acids. Water dissolves out neutral tellurate from the yellow mass. The insoluble salt is named, by Berzelius, the *alpha-quadritellurate* of potash. The elements of this compound are united by a powerful affinity. It is formed when hydrated telluric acid is intimately mixed with a potash-salt, such as nitre or chloride of potassium, and the mixture calcined at a temperature which should be much below a red heat; also when tellurous acid is ignited with chlorate of potash, and in other circumstances. Hydrate of potash dissolves the alpha-quadritellurate by fusion, and nitric acid by a long continued ebullition; but, in both cases, the acid set free in the solution exhibits the properties of ordinary telluric acid.

Telluretted hydrogen, Hydrotelluric acid, TeH, is a gaseous compound of tellurium and hydrogen, analogous in constitution and properties to sulphuretted hydrogen. It is obtained by fusing tellurium with zinc or with tin, and acting on the mixture with hydrochloric acid.

Definite *sulphides of tellurium* have been obtained, corresponding with tellurous and telluric acids. They are sulphur-acids.

Two *chlorides of tellurium* have been formed, a protochloride, $TeCl$, to which there is no corresponding oxide, and a bichloride, $TeCl_2$. No higher chloride, corresponding with telluric acid, has been obtained.

Tellurium forms alloys with several metals, *e. g.*, with potassium, sodium, aluminum, bismuth, zinc, tin, lead, iron, copper, mercury, silver, and gold. Some of these alloys, as those of bismuth, silver, and gold, are found native.

Telluride of potassium is prepared by mixing 1 part of tellurium powder with 10 parts of burnt tartar; introducing the mixture into a porcelain retort fitted with a glass tube bent downwards at right angles; heating the retort to redness for three or four hours, as long, indeed, as carbonic oxide continues to escape; and then introducing the end of the bent tube into a flask kept full of carbonic acid gas, to prevent access of air; this latter precaution is necessary on account of the highly pyrophoric character of the product (Wöhler). The compound may also be obtained by heating tellurium with potassium, in a retort filled with hydrogen; combination then takes place attended with vivid combustion. Telluride of potassium dissolves in water, forming a port-wine coloured solution, which on exposure to the air becomes decolorized, and deposits tellurium in shining scales; with acids it evolves telluretted hydrogen gas. *Telluride of sodium* is prepared by similar methods, and possesses similar properties.

ESTIMATION OF TELLURIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

When tellurium exists in solution in the form of tellurous acid it is reduced to the metallic state by sulphurous acid or an alkaline bisulphite. The reduced tellurium is then collected on a weighed filter, and carefully dried at gentle heat. If the solution is alkaline, it must be previously acidulated with hydrochloric acid; if it contains nitric acid, which might redissolve a portion of the precipitated tellurium, it must be boiled with hydrochloric acid till all the nitric acid is decomposed, then diluted with water, and treated with sulphurous acid as above. If the tellurium is in the state of telluric acid, that compound must first be reduced to tellurous acid by boiling with hydrochloric acid, and the tellurium then reduced by sulphurous acid.

Tellurium may be separated from the *alkalies* and *earths*, and from *manganese*, *iron*, *cobalt*, *nickel*, *zinc*, and *chromium*, by means of hydrosulphuric acid. If the precipitated sulphide of tellurium is quite pure and definite, it may be collected on a weighed filter, dried and weighed, and the amount of tellurium calculated from it. But if it contains excess of sulphur, which is often the case, it must be boiled with aqua-regia till it is completely decomposed; the solution filtered from the separated sulphur; freed from nitric acid in the manner above described; and the tellurium precipitated by sulphurous acid.

The separation of tellurium from *cadmium*, *copper*, and *lead*, may be effected by means of sulphide of ammonium, in which the sulphide of tellurium is easily soluble. The filtered solution is then treated with excess of hydrochloric acid to precipitate the sulphide of tellurium, which is then decomposed by aqua-regia as just described. Tellurium may be separated from *tin* in solution by means of sulphurous acid.

The quantity of metallic tellurium in an alloy may be estimated by heating the alloy in a current of chlorine gas; passing the volatile chloride of tellurium into water acidulated with hydrochloric acid, which dissolves it; and reducing the tellurium by sulphurous acid.

ORDER VI.

METALS ISOMORPHOUS WITH PHOSPHORUS.

SECTION I.

ARSENIC.

Eq. 75 *or* 937·5.

This metal is found native, but more generally in combination with other metals, particularly cobalt and nickel, and is largely condensed, during the roasting of their ores, in the state of arsenious acid. The metal may be easily obtained, in a state of purity, by subliming a portion of native arsenic in a glass tube or retort, by the heat of a lamp, or by reducing a mixture of one part of arsenious acid and three parts of black flux, in the same apparatus. The metal in condensing forms a crust, of a steel-grey colour and bright metallic lustre. It has been observed to crystallize by sublimation in rhombohedral crystals, and is isomorphous with tellurium and antimony. It is a brittle metal, and very easily pulverized. The density of arsenic is from 5 to 5·96. It rises in vapour at 356° (180° Cent.) without first undergoing fusion. Arsenic vapour is colourless; its density is 10·370; and, like phosphorus and oxygen, its combining measure is one volume. It has as strong an effect upon the organ of smell as selenium; its odour resembles that of garlic. Arsenic combines in three proportions with oxygen, forming by spontaneous oxidation in air a grey sub-oxide, the composition of which is undetermined; it also forms arsenious and arsenic acids, AsO_3 and AsO_5.

Arsenious acid, 99 *or* 1237·5. — This compound is formed when metallic arsenic is volatilized in contact with the air. It is obtained in large quantity, as an accessary product, in the roasting of arsenical ores of tin, cobalt, and nickel, and as principal product in the roasting of arsenical pyrites. These operations are performed in reverberatory furnaces, communicating with chambers in which the arsenious acid condenses. The product is purified by a second sublimation in vessels of cast-iron, or, on a small scale, in glass or earthen retorts.

Arsenious acid heated in a tube closed at both ends melts into a colourless liquid; but under the ordinary atmospheric pressure, it volatilizes at about 380° (at 444° according to Mitchell), without previous fusion, producing a colourless vapour, which has a density of 13·850, and is therefore composed of 1 volume of arsenic vapour and 3 volumes of oxygen, condensed into 1 volume. The vapour is inodorous when pure, but if the acid be volatilized in contact with any easily oxidizable substance, as when it is thrown on red-hot coals or iron, the garlic odour of metallic arsenic becomes perceptible.

In the solid state, arsenious acid exhibits three modifications, one amorphous, and two crystalline. (1.) When the sides of the vessel in which the acid is distilled become strongly heated, the vapour condenses, at a temperature near the melting point of the acid, into a transparent vitreous mass, having a conchoïdal fracture. (2.) When arsenious acid is sublimed in a glass tube, or under any circumstances which allow the vapour to condense suddenly, and solidify at once, without passing through the semi-fused state, it assumes the form of regular octohedrons, which, if the sublimation be slowly conducted, are distinct, and have an adamantine lustre. Similar octohedral crystals are obtained when arsenious acid separates from its solution in water or in ammonia. (3.) In the roasting of arsenical cobalt ores, arsenious acid is sometimes obtained in the form of thin transparent flexible plates, derived from a right rhombic prism (Wöhler). Crystals of similar form are obtained by saturating a boiling solution of caustic potash with arsenious acid, and then leaving it to cool, or mixing it with water (Pasteur). Vitreous arsenious acid, even when completely protected from air and moisture, gradually loses its transparency, and becomes an opaque white mass, passing in fact into the octohedral variety.

The specific gravity of transparent vitreous arsenious acid is 3·7385, that of the octohedral variety 3·699 (Guibourt). The vitreous acid dissolves in water more quickly and more abundantly than the opaque crystalline acid; the same quantity of water which at 54° or 55° will take up 36 or 38 parts of the former, will not take up more than 12 or 14 of the latter (Bussy). According to Guibourt, on the contrary, 100 parts of boiling water dissolve 9·68 parts of the vitreous, and 11·47 of the opaque acid; and when the solutions are left to cool to 60°, the first retains 1·78 parts, and the latter 2·9 parts of the acid. The discrepancy of these statements and of various others respecting the solubility of arsenious acid, may perhaps be reconciled by the great facility with which the amorphous variety passes into the crystalline, and *vice versâ*. It appears indeed that heat tends to transform the opaque into the vitreous acid, and cold to produce the contrary change, and this tendency is manifested even in presence of water. Thus the opaque acid is converted into the vitreous by long boiling with water, the contrary change taking place gradually in the solution when cold.

The aqueous solution of arsenious acid is transparent and colourless, and reddens litmus slightly. *Hydrosulphuric acid* colours it yellow, and on the addition of hydrochloric acid throws down a yellow precipitate of AsS_3. On the addition of a small quantity of ammonia, it gives a yellow precipitate with nitrate of *silver*, and a peculiar light green (Scheele's green) with sulphate of *copper;* these precipitates are easily soluble in excess of ammonia. Mixed with hydrochloric acid it produces a grey metallic deposit on *copper*. With *zinc* and sulphuric or hydrochloric acid, it evolves arseniuretted hydrogen gas (p. 533).

Arsenious acid dissolves in many acids, in hydrochloric acid for example, with much greater facility than in water, but without forming any definite compounds. It is dissolved, however, by bitartrate of potash, with formation of a crystallizable salt analogous to the potash-tartrate of antimony. The vitreous acid dissolved in boiling dilute hydrochloric acid crystallizes on cooling in regular octohedrons, the deposition of each crystal being accompanied by a flash of light. Agitation increases the number of crystals produced, and the intensity of the light. The opaque acid dissolved in hydrochloric acid does not emit any light on crystallizing; the same is the case with the crystals obtained by cooling a solution of the vitreous acid in hydrochloric acid, when these crystals are redissolved in hydrochloric acid. Hence it appears that the vitreous acid dissolves *as such* in hydrochloric acid, and that the emission of light at the moment of crystallization is due to the change from the amorphous to the crystalline state.

Arsenious acid is dissolved by *potash*, *soda*, and *ammonia*, also by *alkaline carbonates*, but from these latter solutions it is sometimes deposited in the free state, so that it is doubtful whether arsenious acid displaces carbonic acid in the humid way. The arsenites of the earths and metallic oxides are insoluble in water, but soluble in acids.

With potash, arsenious acid forms the salts $2KO . AsO_3$, $KO . AsO_3$, and $KO . HO . 2AsO_3$; similar salts with soda. With baryta, it forms $2BaO . AsO_3$, and $BaO . AsO_3$; and with lime, $2CaO . AsO_3$. With nickel, cobalt, and silver, it forms bibasic and sesquibasic salts.

The neutral solutions of the alkaline arsenites give a yellow precipitate with nitrate of *silver*, and Scheele's green with *copper* salts. Acidulated with hydrochloric acid, they give with *hydrosulphuric acid*, &c., the same reactions as aqueous arsenious acid.

Nitric acid and *aqua regia* transform arsenious into arsenic acid. *Hydrogen, charcoal,* and other reducing agents easily reduce it to the metallic state.

Arsenious acid has a rough taste, slightly metallic, and afterwards sweetish. It is one of the most violent among acrid poisons.

The principal industrial use of arsenious acid is in calico-printing; it is also used in glass-making, serving to transform the protoxide of iron into sesquioxide, which produces glasses less highly coloured than the protoxide.

Arsenic acid, AsO_5, 115 *or* 1437·5.—This acid is obtained by heating powdered arsenious acid in a basin with an equal quantity of water, and adding nitric acid in small quantities to the mixture at the boiling point, so long as ruddy fumes escape. An addition of hydrochloric acid to the water is generally made, to increase the solubility of the arsenious acid, but it is not absolutely necessary. The solution of arsenic acid is then evaporated to dryness, to expel the remaining nitric and hydrochloric acids; but the dry mass must not be heated above the melting point of lead, otherwise oxygen gas is emitted and arsenious acid reproduced. Arsenic acid thus obtained is milk-white, and contains no water. Exposed to air, it slowly deliquesces, and runs into a liquid. But notwithstanding this, when strongly dried, it does not dissolve completely in water at once, and a portion of it appears to be insoluble; but the whole is dissolved by continued digestion. Arsenic acid, in absorbing moisture from the air, sometimes forms hydrated crystals, which are highly deliquescent; but this acid is easily made anhydrous, and does not retain basic water with force, like phosphoric acid. Its solution has a sour taste. and reddens vegetable blues. Arsenic acid, indeed, is a strong acid, and with the aid of heat expels all the volatile acids from their combinations. Arsenic acid undergoes fusion at a red heat, and at a higher temperature is completely dissipated in the form of arsenious acid and oxygen.

When an equivalent of arsenic acid is ignited with an excess of carbonate of soda, three equivalents of carbonic acid are expelled, and a *tribasic arseniate of soda* formed, which when dissolved in water, crystallizes with 24 equivalents of water, forming the salt $3NaO \cdot AsO_5 + 24HO$, isomorphous with the subphosphate of soda. The same salt is obtained by treating arsenic acid in solution with an excess of caustic soda. When carbonate of soda is added to a hot solution of arsenic acid, so long as there is effervescence, a salt is obtained by evaporation corresponding with the common phosphate of soda, containing 2 eq. of soda and 1 eq. of water as bases. This salt affects the same two multiples, in its water of crystallization, as phosphate of soda, namely, 24HO and 14HO, but most frequently assumes the smaller proportion, forming the salt $2NaO \cdot HO \cdot AsO_5 + 14HO$. This arseniate is more soluble than the phosphate, and slightly deliquescent in damp air. When to the last salt a quantity of arsenic acid is added equal to that which it already contains, and the solution is highly concentrated, the salt named *biarseniate of soda* crystallizes at a low temperature. This salt contains 1 eq. of soda and 2 eq. of water as bases, with 2 eq. of water of crystallization, and corresponds with the biphosphate of soda. Its formula is $NaO.2HO.AsO_5 + 2HO$. The *biarseniate of potash,* which is analogous in composition, is a highly crystallizable salt. It is sometimes prepared by deflagrating arsenious acid with an equal weight of nitrate of potash. These arseniates of the alkalies, which contain water as base, all lose that element at a red heat; but, unlike the phosphates, they recover it when redissolved in water. Arsenic acid, therefore, forms only one, and that a tribasic class of salts. The arseniates of the earths and other metallic oxides are insoluble in water, but soluble in acids. *Arseniate of silver* ($3AgO \cdot AsO_5$) falls as a precipitate of a chocolate-brown colour, when nitrate of silver is added to the solution of an arseniate, and affords an indication of the presence of arsenic acid. On treating a solution of arsenic acid with *ammonia* in excess, *chloride of ammonium,* and *sulphate of magnesia,* a white crystalline precipitate is formed, consisting of arseniate of magnesia and ammonia, $2MgO \cdot NH_4O \cdot AsO_5 + 12Aq.$, similar in appearance and analogous in constitution to the ammonio-magnesian phosphate.

Hydrosulphuric acid produces a yellow precipitate of AsS_5 after a considerable time; but if the solution be previously mixed with sulphurous acid, which reduces the arsenic acid to arsenious acid, a precipitate of AsS_3 is immediately produced.

Sulphides of arsenic.—When the bisulphide, realgar, is digested in caustic potash, it gives off sulphur and leaves a brownish black powder, having some resemblance to bioxide of lead, which, according to Berzelius, is the sulphide As_6S. *Bisulphide of arsenic,* AsS_2, is obtained by fusing sulphur with an excess of arsenic or arsenious acid. It is transparent and of a fine ruby colour after cooling, and may be distilled without decomposition. It forms the crystalline mineral realgar. *Sulpharsenious acid,* or *orpiment,* AsS_3, also occurs native. It may be prepared by decomposing a solution of arsenious acid in hydrochloric acid, hydrosulphuric acid, or by an alkaline sulphide. This sulphide has a rich yellow colour, and is the basis of the pigment called *king's yellow.* It is insoluble in acids, but soluble to a small extent in water containing hydrosulphuric acid, and also in pure water, but is precipitated by ebullition with a little hydrochloric acid. When heated, it fuses readily and becomes crystalline on cooling. It is readily dissolved by ammonia and solutions of the fixed alkalies, and is indeed a powerful sulphur-acid. *Sulpharsenic acid,* AsS_5, falls as a yellow precipitate, having much the appearance of orpiment, when a solution of arsenic acid somewhat concentrated is decomposed by hydrosulphuric acid. It may be sublimed without change, and after cooling forms a non-crystalline mass. It is also a powerful sulphur-acid, forming salts called *sulpharseniates. Persulphide of arsenic,* AsS_{18}, is obtained by precipitating neutral solution of sulpharseniate of potassium with alcohol, filtering the liquid, and evaporating off two-thirds of the alcohol; the concentrated solution, when left to cool, deposits the persulphide of arsenic in shining yellow crystalline laminæ.

Chlorides of arsenic.—A *terchloride,* $AsCl_3$, corresponding with arsenious acid, is formed when arsenic is introduced into chlorine gas, in which it takes fire and burns spontaneously. The same compound is obtained by distilling a mixture of 1 part of arsenic with 6 parts of corrosive sublimate; also by distilling arsenious acid with excess of hydrochloric acid, or of common salt and sulphuric acid. It is a colourless, oily, and very dense liquid, which is resolved by water into arsenious and hydrochloric acids. When a mixture of arsenic and calomel is distilled, a dark brown sublimate is formed, consisting partly of Hg_2ClAs, partly of Hg_4ClAs. No chloride corresponding with arsenic acid is known. *Bromide of arsenic,* $AsBr_3$, is formed by the direct combination of its elements. *Iodide of arsenic,* AsI_3, is formed, according to Plisson, by digesting 3 parts of arsenic with 10 of iodine and 100 of water, as long as the odour of iodine is perceived. The liquid yields by evaporation red crystals of the iodide. *Fluoride of arsenic,* AsF_3, is obtained by distilling a mixture of fluor spar and arsenious acid with sulphuric acid. It is a fuming, colourless liquid; the density of its vapour is 2730 (Unverdorben).

Arsenic and hydrogen.—A solid arsenide of hydrogen was obtained by Davy, by using metallic arsenic as the negative pole (the chloroid) in decomposing water. Gay-Lussac and Thénard have also shown that the same compound precipitates when arsenide of potassium is dissolved in water. It is a chestnut-brown powder, which may be dried without change. Its composition has not been determined with accuracy. *Arseniuretted hydrogen,* AsH_3, a gas analogous in constitution to ammonia, is obtained by dissolving arseniate of potassium or sodium in water, or an alloy of equal parts of zinc and arsenic in sulphuric acid diluted with three times its weight of water; or again, when zinc dissolves in hydrochloric or dilute sulphuric acid, with which arsenious acid is mixed:

$$6Zn + 3HO + AsO_3 + 6SO_3 = 6(ZnO.SO_3) + AsH_3.$$

It is a dangerous poison, when inhaled even in the most minute quantity, and should, therefore, be prepared with the greatest caution. The density of this gas is 2695 (Dumas). It is liquefied by a cold of —40°. When passed through a glass tube heated to redness by a spirit lamp, it is decomposed and deposits metallic arsenic. The flame of this gas, when burned in air, also deposits metallic arsenic upon a cold object exposed to it. No combination of arseniuretted hydrogen is known with either acids or bases. It precipitates many of the metallic solutions which are precipitated by hydrosulphuric acid, but not oxide of lead, its hydrogen alone being oxidated, and the arsenic being precipitated in combination with the metal. From the salts of silver, gold, platinum, and rhadium, it precipitates the metals, while arsenious acid remains in solution. This gas, when pure, is completely absorbed by a solution of sulphate of copper, and $AsCu_3$ precipitated.

TESTING FOR ARSENIC.

Poisoning from arsenious acid is much more frequent than from any other substance. Hence, a more than usual degree of importance is attached to the modes of detecting the presence of arsenic in minute quantity. Of the different preparations of the metal, arsenic acid, and after it arsenious acid, are the most poisonous; the salts and sulphides are so in a much less degree. Arsenious acid in the solid form and unmixed with foreign matters, is easily recognized as a white heavy powder, which is tasteless or nearly so, is entirely volatilized by heat, and diffuses a garlic odour in the reducing flame of a lamp. When dissolved in water, arsenious acid may be detected by the fluid tests, already mentioned (p. 531). The silver and copper tests are most conveniently applied in the following forms.

1. *Ammonio-nitrate of silver.*—This is an exceedingly delicate test of arsenious acid, whether free, or in combination with an alkali. It is prepared by adding diluted ammonia to a solution of nitrate of silver, till the oxide of silver, which is first thrown down, is redissolved. When the ammonia has been added in proper quantity and not in excess, the odour of that substance is scarcely perceptible, and the liquid contains in solution the crystallizable ammonio-nitrate of silver, $AgO.NO_5.2NH_3$. This test-liquid throws down from arsenious acid, the yellow arsenite of silver, which is redissolved both by acids and by ammonia. A solution of nitrate of silver gives the same indication as the prepared ammonio-nitrate in an alkaline but not in an acid solution of arsenious acid. Nitrate of silver produces, in phosphate of soda or any other soluble phosphate, a yellow precipitate of phosphate of silver of the same colour as the arsenite of silver, and which might, therefore, be mistaken for the latter; but the action of the ammonio-nitrate is not liable to that ambiguity, as it does not produce a yellow precipitate in an alkaline solution of phosphoric acid, the phosphate of silver being then retained in solution by the ammonia of the reagent, although arseniate of silver is precipitated in the same circumstances. Both phosphate and arseniate of silver are indeed considerably more soluble in ammonia than the arsenite of the same metal.

2. *Ammonio-sulphate of copper* gives a beautiful green precipitate, the arsenite of copper, in both alkaline and acid solutions of arsenious acid; sulphate of copper gives the same precipitate in the former, but not in the latter.

But in solutions containing organic matter, the indications of these tests are sometimes delusive, and often doubtful. Recourse is then had to the proper means of obtaining arsenic in the metallic form, from the liquid suspected to contain arsenious acid. Indeed, even where the indications of the fluid tests are clear, the reduction test should never be omitted, the evidence which it affords being of a superior and completely demonstrative character. The reduction test of arsenic is practised in two different ways: (1) by the reduction of the sulphide of arsenic by means of charcoal and carbonate of potash, and (2) by the production, and subsequent decomposition of the gaseous compound of arsenic and hydrogen. The following operations are necessary in the practice of the first method:—

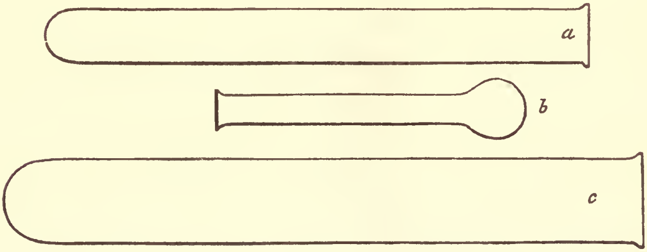
REDUCTION TEST OF ARSENIC.

I. Preparation of the fluid:
  1. Heat the mass with about one-fourth of its weight of strong sulphuric acid in a retort, to which is adapted a receiver having its inner surface wetted, till the organic matter is carbonized.
  2. Pulverize the residue, and treat it with nitric acid mixed with a little hydrochloric acid, in order to bring the arsenic to the state of arsenic acid, which is easily soluble.
  3. Boil with water; filter; and mix the filtrate with the liquid in the receiver.*

II. Precipitation of the sulphide of arsenic:
  1. Transmit a stream of hydrosulphuric acid gas through the liquid for half an hour.†
  2. Heat the liquid in an open vessel for a few minutes, to cause the precipitate to separate.
  3. Wash the precipitate by affusion of water acidulated with hydrochloric acid, and subsidence.
  4. Dry the precipitate at a temperature not exceeding 300°.

III. Reduction of the sulphide of arsenic:
  1. Mix the dried precipitate intimately with twice its bulk of dry black flux (carbonate of potash and charcoal), or with a mixture of pounded charcoal and dry carbonate of soda, or with cyanide of potassium, and heat to redness in a glass tube, of the form and size of *a* or *b*, exhibited below.
  2. Heat slowly a particle of the metallic crust in a glass tube *c*, and observe the formation of a white crystalline sublimate of arsenious acid.
  3. Dissolve the sublimate in a small quantity of boiling water, and test with ammonio-nitrate of silver, &c., as above

FIG. 193.



Marsh's test. — Hydrogen cannot be evolved in contact with any preparation of arsenic, soluble or insoluble, without combining with the metal, which is thus removed from the liquor, in the form of arseniuretted hydrogen gas. Mr. Marsh has founded, upon this fact, a simple and elegant mode of obtaining metallic arsenic from arsenical liquors. The stopcock being removed from the bulb-apparatus represented in the figure, a fragment of zinc is placed in the lower bulb,

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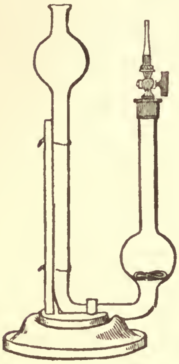
* This is the mode of preparation most generally adopted, and it is applicable to all cases of searching for mineral poisons. Another method, which is especially applicable when the matter to be examined contains a large quantity of fat, is to heat the mass with strong hydrochloric acid, or aqua-regia, in a large retort; the greater part of the arsenic is then converted into chloride, and may be collected in a receiver containing water.

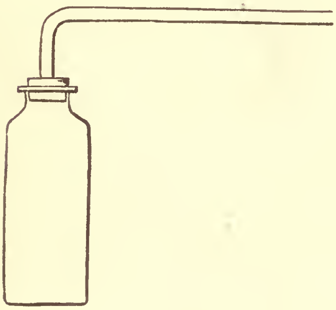
† As the arsenic is in the state of arsenic acid, it is best to mix the liquid with sulphurous acid before passing the hydrosulphuric acid gas through it.

FIG. 194.



and diluted sulphuric acid poured upon it. The stopcock being replaced and closed, the lower bulb is soon filled with hydrogen gas, and the acid liquid forced into the upper bulb. It is necessary to test this hydrogen for arsenic, which will be found in it, if the zinc itself contains that metal. The gas for this purpose is kindled at the stopcock and allowed to burn with a small flame. If a stoneware plate be depressed upon the flame, a black spot of steel-grey colour and bright metallic lustre, is formed, in a few seconds, upon the surface of the plate, supposing the gas to contain arsenic; or if a cold piece of glass be held over the flame, at a small height above it, a white sublimate of arsenious acid condenses upon the glass. But if the zinc employed contains no arsenic, neither of these effects is produced. The zinc being proved to be free from arsenic, a portion of the liquor to be tested is introduced into the lower bulb, in addition to the acid and zinc already there; and when the bulb is again filled with hydrogen gas, the latter is burned and examined precisely as before. If the liquor is loaded with organic matter, as generally happens with the liquids submitted to examination in actual cases of poisoning, the gas may be filled with froth, and the evolution of it very slow. But in the course of a night, the gas is generally obtained in sufficient quantity, and in a proper state, to permit of examination. It is much better, however, first to remove the organic matter by one of the methods above given; the gas is then evolved freely and without frothing, and a plain bottle with a cork and glass jet will be sufficient for this reduction experiment. Then also, instead of burning the gas at the jet, it may be allowed to escape by a horizontal tube, such as that in figure 195, a portion of which is heated to redness by a spirit lamp. The arsenic condenses within the tube, beyond the flame and nearer the aperture, and forms a metallic crust, which may be converted by sublimation into arsenious acid; the sublimate may then be dissolved in a small quantity of boiling water, and the solution tested with ammonio-nitrate of silver, &c., as before.

FIG. 195.



When the liquid examined contains antimony, that metal combines with the nascent hydrogen, and comes off as antimoniuretted hydrogen, a gas which, when burned, or heated in a glass tube, gives the metal and a white sublimate, in the same circumstances as arsenic (L. Thompson). Antimony, however, may be recognised by a peculiarity of its reduction in the ignited tube. This metal is deposited in the tube, on both sides of the heated portion of it, and closer to the flame than arsenic, owing to the inferior volatility of antimony. The white sublimate also, if dissolved in water containing a drop of ammonia, will not give the proper indications with the fluid tests of arsenic, if the metal be antimony. Another distinction is, that the arsenical deposit is soluble in hypochlorite of soda, whereas the antimonial deposit is not.

Antidotes to arsenious acid.—When hydrated sesquioxide of iron is mixed with a solution of arsenious acid to the consistence of a thin paste, a reaction occurs by which the arsenious acid disappears in a few minutes, and the mass ceases to be poisonous. The arsenious acid takes oxygen from the sesquioxide of iron, and becomes arsenic acid, while the sesquioxide of iron is reduced to protoxide, a protarseniate of iron being the result, which is insoluble and inert:

$$2Fe_2O_3 + AsO_3 = 4FeO . AsO_5.$$

The constitution of this arseniate of iron is probably $2FeO . HO . AsO + 2FeO$. Sesquioxide of iron, when used as an antidote to arsenious acid, should be in a gelatinous state, as it is obtained by precipitation, without drying. It may be prepared extemporaneously, by adding bicarbonate of soda in excess to any tincture or red solution of iron. Calcined magnesia may likewise be used as an antidote to arsenic. Care should be taken in preparing the latter not to employ too great a heat, which would render it very dense, and cause it to combine but slowly with the arsenious acid.

ESTIMATION OF ARSENIC, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

When arsenic is contained in a solution entirely in the form of arsenic acid, the best mode of estimating it is to precipitate it in the form of ammonio-magnesian arseniate, $2MgO . NH_4O . AsO_5 + 12HO$. The solution is mixed with excess of ammonia, and then with sulphate of magnesia, to which a quantity of chloride of ammonium has been added, sufficient to prevent the precipitation of the magnesia by ammonia. The liquid is then left to stand for about twelve hours; the precipitate collected on a weighed filter; washed with water containing ammonia; and dried over sulphuric acid in vacuo at ordinary temperatures; it has then the composition expressed by the above formula. It may also be dried, and more expeditiously, by exposing it to a temperature of exactly 212° F., whereby it loses 11 eq. of water, and is reduced to $2MgO.NH_4O.AsO_5 + HO$. Exposure to a higher temperature occasions loss of arsenic.

If the liquid contains arsenious acid, that compound may be converted into arsenic acid by mixing the solution with hydrochloric acid, and adding chlorate of potash by small quantities. The vessel must be left in a moderately warm place till the odour of free chlorine has entirely disappeared. Aqua regia may also be used to effect the oxidation, but it is less convenient. In either case, the liquid must be considerably diluted with water, otherwise part of the arsenic will be converted into chloride, and volatilized. It is best, perhaps, to perform the oxidation in a capacious retort having a receiver adapted to it.

Arsenious acid may also be estimated by its action on terchloride of gold. The arsenious acid is thereby converted into arsenic acid, and gold is precipitated in the metallic state. The quantity of gold thus reduced gives the quantity of arsenious acid present:

$$2AuCl_3 + 6HO + 3AsO_3 = 2Au + 6HCl + 3AsO_5.$$

The gold solution used for the purpose is the sodio-chloride, or ammonio-chloride of gold. It must be free from nitric acid; but the presence of hydrochloric acid, even in large excess, does not interfere with the action. The liquid, after the addition of the arsenic solution, must be left to itself for a considerable time to enable the gold to settle down completely.

When arsenic and arsenious acids exist together in solution the former may be precipitated as ammonio-magnesian arseniate (a considerable quantity of sal-ammoniac being added to prevent the simultaneous precipitation of the arsenious acid); the arsenious acid converted into arsenic acid by oxidation with chlorate of potash and hydrochloric acid, and then precipitated in a similar manner; or the arsenious acid may be estimated by chloride of gold, as last described.

The separation of arsenic in solution from the alkalies, earths, and those metals which are not precipitated from their acid solutions by hydrosulphuric acid, is effected by passing a stream of that gas through the acid liquid for a considerable time, then leaving it to stand, and heating it gently to ensure the complete precipitation of the sulphide of arsenic. If the arsenic is in the form of arsenic acid, that compound must be previously reduced to arsenious acid by means of sulphurous acid. The tersulphide of arsenic is collected on a weighed filter, thoroughly washed, and dried at a moderate heat. If quite pure, it may be weighed with the filter, and the quantity of arsenic thereby directly determined. But as it almost always contains an excess of sulphur, it is better to take a weighed quantity of it from the filter, oxidize it in a capacious flask by means of dilute hydrochloric acid and chlorate of potash, continuing the operation till the greater part of the sulphur is converted into sulphuric acid, and the remainder collects at the bottom of the liquid in a compact yellow globule; then decant the liquid, wash the globule of sulphur, and weigh it; and, finally, estimate the quantity of sulphur in the solution by precipitation with chloride of barium, adding the quantity thus found to the weight of the globule. The proportion of sulphur in the precipitated sulphide of arsenic being thus ascertained, the amount of arsenic is easily calculated.

From *cadmium*, *copper*, and *lead*, arsenic may be separated by means of sulphide of ammonium. The filtered ammoniacal solution is then treated with excess of hydrochloric or acetic acid to throw down the sulphide of arsenic, and the precipitate treated in the manner just described.

The separation of arsenic from *tin* is attended with considerable difficulty. One of the best methods is to convert the two metals into sulphides, and separate them, after drying and weighing the whole, by ignition in a stream of hydrosulphuric acid gas. The mixed sulphides are introduced into a weighed glass bulb, having a tube attached to it on each side. One of these tubes, the exit-tube, must be at least a quarter of an inch in diameter, to prevent stoppage, and bent downwards so as to dip into a flask containing ammonia. The whole is then weighed, hydrosulphuric acid gas passed through the apparatus, and the bulb heated till the whole of the sulphide of arsenic is sublimed. Part of the sulphide of arsenic passes into the ammoniacal liquid, by which it is dissolved, and the rest sublimes in the wide tube. When the operation is ended, and the apparatus has cooled, the wide tube is cut off at a short distance from the bulb, then broken, and the pieces digested in caustic potash to dissolve out the sulphide of arsenic. The solution thus obtained is added to the ammoniacal liquid in the flask; the sulphide of arsenic precipitated by hydrochloric acid, oxidized without previous filtration with hydrochloric acid and chlorate of potash; and the resulting arsenic acid precipitated by ammonia and sulphate of magnesia. The sulphide of tin remaining in the bulb is converted into stannic oxide by treating it with strong nitric acid.

When arsenic is combined with other metals in the form of an alloy, the whole may be dissolved or oxidized by means of aqua regia, or, better, with hydrochloric acid and chlorate of potash, and the arsenic separated by one of the preceding methods. In the case of tin, however, it is best to fuse the alloy in thin laminæ with five times its weight of carbonate of soda and an equal quantity of sulphur, whereby a mixture of sulpharseniate and sulphostannate of soda is obtained, which dissolves completely in hot water. The sulphides of tin and arsenic may then be precipitated by hydrochloric acid, and separated as above.*

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* For a full account of the methods of estimating arsenic and separating it from other metals, *vide* H. Rose, "Handbuch der analytischen Chemie," 1851, ii. 381.

SECTION II.

ANTIMONY.

Eq. 120·24 *or* 1503*; Sb (*stibium*).

This metal was well known to the alchemists, and is one of the metals the preparations of which were first introduced into medicine. Its sulphide is not an uncommon mineral, and is the source from which the metal and its compounds are always derived.

The sulphide of antimony is easily reduced to the metallic state by mixing together 4 parts of that substance, 3 parts of crude tarter, and 1½ parts of nitre, and projecting the mixture by small quantities at a time into a red hot crucible. The sulphide is also sometimes reduced by fusion with small iron nails, which combine with the sulphur, and disengage the antimony. Or it may be obtained in a state of greater purity by strongly igniting in a crucible a quantity of the potash-tartrate of antimony, and placing the resulting metallic mass in water to remove any potassium it may have acquired.

Antimony is a white and brilliant metal, generally possessing a highly lamellated structure. It is easily obtained in rhombohedral crystals of the same form as arsenic and tellurium. Its density is from 6·702 to 6·86. It undergoes no change in the air. The point of fusion of antimony is estimated at 797°; it may be distilled at a white heat. This metal burns in air at a red heat, and produces copious fumes of oxide of antimony.

Antimony combines in three proportions with oxygen, forming oxide of antimony and antimonic acid, SbO_3 and SbO_5, which correspond respectively with arsenious and arsenic acids; and antimonious acid, SbO_4, which is probably an intermediate or compound oxide, analogous to the black oxide of iron.

Teroxide of antimony, Antimonic oxide, Antimonious acid, SbO_3, 144·24 or 1803. — This oxide may be obtained by dissolving the sulphide, finely pounded and in the condition in which it is known as prepared sulphide of antimony, in four times its weight of concentrated hydrochloric acid. Pure hydrosulphuric acid goes off, and the antimony is converted into terchloride:

$$SbS_3 + 3HCl = SbCl_3 = 3HS.$$

The clear solution may be poured off, and precipitated at the boiling heat by a solution of carbonate of potash added in excess; the carbonic acid, which does not combine with oxide of antimony, escaping as gas. Teroxide of antimony, so prepared, is anhydrous, but is slightly soluble in water: it is white, but assumes a yellow tint when heated. It is fusible at a red heat, and sublimes at a high temperature in a close vessel, where it cannot pass into a higher state of oxidation. The brilliant crystalline needles which condense about antimony in a state of combustion likewise consist of this oxide. They possess the unusual prismatic form of arsenious acid observed by Wöhler. Oxide of antimony also crystallizes as frequently in regular octohedrons, the other form of arsenious acid. It occurs in the prismatic form as a rare mineral, whose density is 5·227.

When a solution of potash is poured upon the bulky hydrate of teroxide of antimony, which is precipitated from the chloride by water, a portion of the oxide is

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* The number 129, given by Berzelius for the equivalent of antimony, and hitherto generally adopted, appears from recent experiments by Schneider (Pogg. Ann. xcviii. 293) and by H. Rose (Berl. Akad. Ber. 1856, p. 229) to be much too high. Schneider, by reducing the tersulphide of antimony with hydrogen, finds the equivalent to be 120·24; and Rose, by decomposing the terchloride with hydrosulphuric acid, and precipitating the chlorine with nitrate of silver, finds the number 120·69.

dissolved, but the greater part loses its water, and is reduced in a few seconds to a fine greyish, crystalline powder, which is a neutral combination of teroxide of antimony with potash. Teroxide of antimony also combines with acids, forming the *salts of antimony* or *antimonic salts.*

The solution of these salts give with *hydrosulphuric acid* a brick-red precipitate of tersulphide of antimony, easily soluble in sulphide of ammonium, and reprecipitated by acids. This precipitate dissolves in strong boiling hydrochloric acid, forming the terchloride, which when thrown into water yields a precipitate of the oxychloride. This reaction with hydrosulphuric acid distinguishes antimony from all other metals.[*] *Zinc* or *iron* precipitates antimony from its solutions in the form of a black powder, which, when fused on charcoal before the blow-pipe, yields a brittle button of the metal. According to Dr. Odling,[†] antimony is also precipitated by *copper,* in the form of a brilliant metallic film, which may be dissolved off the copper by a solution of permanganate of potash, yielding a solution which will give the characteristic red precipitate with hydrosulphuric acid. This reaction affords a ready method of separating antimony from liquids containing organic matter,—as in medico-legal inquiries. All compounds of antimony fused upon charcoal with *carbonate of soda* or *cyanide of potassium,* yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of antimonic oxide. The reduction with cyanide of potassium may also be performed in a porcelain crucible, without charcoal. A solution of *terchloride of gold* added to the solution of a salt of teroxide of antimony, forms a yellow precipitate of metallic gold, the oxide of antimony being at the same time converted into antimonic acid, which compound is precipitated as a white powder, together with the gold, unless the solution contains a very large excess of hydrochloric acid. In a solution of oxide of antimony in potash, terchloride of gold produces a black precipitate, which is not altered by heating. This reaction is extremely delicate.

Tersulphide of antimony, SbS_3, 168·24 or 2103.—The common ore of antimony is a tersulphide, SbS_3, corresponding with the preceding oxide of antimony. It is rarely free from sulphide of arsenic, which thus often enters into the antimonial preparations derived from the sulphide of antimony, but into tartar-emetic less frequently than the others. The same sulphide is formed when salts of the oxide of antimony, such as tartar-emetic, are precipitated by hydrosulphuric acid; but it is then of an orange-red colour. When the precipitated sulphide is dried, it loses water and becomes anhydrous, still remaining of a dull orange colour; but when heated more strongly, it shrinks at a particular temperature, and assumes the black colour and metallic lustre of the native sulphide. This sulphide is also obtained of a dark brown colour by boiling the prepared sulphide of antimony in a solution of carbonate of potash, and allowing the solution to cool; by fusing $2\frac{2}{3}$ parts of the prepared sulphide with 1 part of carbonate of potash; or dissolving it in a boiling solution of caustic potash, and afterwards adding an acid. The last preparation is known as *Kermes mineral.* It has a much duller colour than the precipitated sulphide, but differs from it only in containing small quantities of oxide and pentasulphide of antimony, together with an alkaline sulphide which cannot be removed by washing (Berzelius). When the cooled mother-liquor from which kermes is deposited is mixed with hydrochloric acid, a precipitate is obtained, consisting, like the kermes, of SbS_3 mixed with SbO_3 and SbS_5, but of a redder colour. It is sometimes called the *golden sulphuret of antimony.*

When the sulphide of antimony is oxidated at a red heat, much sulphur is burned off, and an impure oxide of antimony remains. This matter forms, when fused, the *glass of antimony,* which contains a considerable quantity of undecom-

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[*] For the reactions of antimonic salts with alkalies, see *terchloride of antimony* and *tartar-emetic.*

[†] Guy's Hospital Reports, [3.] ii. 249.

posed sulphide. The glass, reduced to powder, is boiled with bitartrate of potash as a source of oxide of antimony, in the pharmaceutical preparation of tartar-emetic. The oxide of antimony is dissolved out from the glass by acids, and a substance is left which is called *saffron of antimony.* This last is a definite compound of oxide and sulphide of antimony, $SbO_3.2SbS_3$, which also occurs as a mineral—namely, red antimony ore.

Terchloride of antimony, $SbCl_3$, is obtained by distilling either metallic antimony or the tersulphide of antimony with corrosive sublimate. When heated it flows like an oil, and becomes a crystalline mass on cooling. It is a powerful cautery. This salt deliquesces in air, and becomes turbid, owing to the deposition of a subsalt. A concentrated solution of chloride of antimony is also obtained by dissolving the sulphide of antimony in hydrochloric acid. When this solution is thrown into water, it gives a white bulky precipitate, which after a time resolves itself into groups of small crystals, having usually a fawn colour; it was formerly called the *powder of Algaroth.* These small crystals are an oxychloride of antimony, which, according to the analyses of Johnston and Malaguti, contains $2SbCl_3.9SbO_3$.

A solution of terchloride of antimony, to which water is added, and then a sufficient quantity of hydrochloric acid to redissolve the precipitate thereby produced, gives with *potash* a white precipitate of the hydrated teroxide, soluble in a very large excess of the alkali. *Ammonia* forms the same precipitate insoluble in excess. *Carbonate of potash,* or *soda,* produces also a white precipitate of the hydrated teroxide, which is soluble in excess, especially of the potash-salt, but reappears after a while. These reactions are greatly modified by the presence of fixed organic acids, especially of tartaric acid. In such a case, water forms no precipitate, ammonia but a slight one and after some time only, and the precipitate formed by potash dissolves easily in excess of the alkali. (See *Tartar-emetic.*)

Terfluoride of antimony, SbF_3, is obtained, by treating the teroxide with strong hydrofluoric acid, in colourless crystals which dissolve in water without decomposition. It unites with fluoride of potassium, forming the compound $3KF.SbF_3$, and similarly with fluoride of sodium and fluoride of ammonium.

Sulphate of antimony, $SbO_3.3SO_3$, is obtained, by boiling metallic antimony with concentrated sulphuric acid, as a white saline mass, which is decomposed by water.

Oxalate of potash and antimony, $KO.C_2O_3+SbO_3.3C_2O_3$. — This is a double crystallizable salt of antimony, which, like the tartrate of potash and antimony, may be dissolved in water without decomposition. It is prepared by saturating binoxalate of potash with oxide of antimony. It is soluble at 48° in ten times its weight of water (Lassaigne). According to Bussy, when binoxalate of potash is digested upon oxide of antimony in excess, two salts are formed, one in oblique prisms, and another less soluble, in intricate small crystals; but neither is very stable. The former is decomposed by a large quantity of water: its analysis gave $3(KO.C_2O_3)+SbO_3.3C_2O_3+6HO$.*

Tartrate of potash and antimony, $KO.SbO_3+C_8H_4O_{10}.2HO$. — This salt, the tartar-emetic, or potash tartrate of antimony of pharmacy, is prepared by neutralizing bitartrate of potash with oxide of antimony: the oxide obtained by decomposing the chloride or sulphate of antimony with water answers best for the purpose. A quantity of oxide of antimony may be boiled with three or four times its weight of water, and bitartrate of potash added in small quantities till the oxide is entirely dissolved. The filtered solution yields the salt, on cooling, in large transparent crystals, the form of which is an octohedron with a rhombic base; they become white in the air, and lose their water of crystallization. They are soluble in 14 times their weight of cold water, and in 1·88 parts of boiling water, but not in alcohol. The mother-liquor of these crystals becomes a syrupy liquid, and dries up into a gummy mass without crystallizing, when oxide of anti-

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* J. Pharm. 1838. p. 509.

mony has been dissolved in excess by the acid tartrate in preparing the salt. *Potash* added to a solution of the salt throws down the teroxide of antimony, but the precipitate is easily soluble in excess of potash. *Ammonia* forms no precipitate at first, and but a slight one after standing. *Alkaline carbonates* form a precipitate of the teroxide insoluble in excess of the reagent. With *hydrosulphuric acid*, the reaction is the same as with other salts of antimony. (See p. 540.) Salts of the earths and basic metallic oxides, such as *baryta* and *oxide of silver*, throw down from its solution a compound of the tartrate of antimony with tartrate of baryta, tartrate of silver, &c. (Wallquist.) Strong acids decompose the salt, and produce a precipitate which is a mixture of bitartrate of potash with oxide of antimony, or with a subsalt of that oxide.

This salt was formerly described as a double tartrate of potash and antimony, or, abstracting its water of crystallization, which is differently stated at 2 and 3 equivalents, as $KO.(C_4H_2O_5) + SbO_3.(C_4H_2O_5)$. When the atomic weight of tartaric acid is doubled, and it is represented as a bibasic acid, the formula for dry tartar-emetic becomes $KO.SbO_3.(C_8H_4O_{10})$. In comparing the last formula with that of bitartrate of potash, represented also as a bibasic salt, $KO.HO.(C_8H_4O_{10})$, it is observed that 1 eq. of oxide of antimony takes the place of 1 eq. of water as base, although the former contains 3 eq. of oxygen, and the latter only one. Tartrate of potash and antimony is, in this respect, an anomalous salt. Another equally remarkable fact respecting this salt has been observed by M Dumas, namely, that 2 eq. of water are separated from the anhydrous salt at 428°, leaving a substance of which the elements are $C_8H_2O_{12}.SbK$. The first part of this formula, $C_8H_2O_{12}$, M. Dumas looks upon as a quadribasic salt-radical, existing in the tartrates, which in hydrated tartaric acid is united with 4H, in bitartrate of potash with $3H+K$, and in tartrate of antimony and potash with $Sb+K$. Here Sb is found equivalent to and capable of replacing 3H. Tartrate of antimony and potash might, therefore, be represented by $KSb(C_8H_2O_{12})+2HO+$ water of crystallization. If SbO_2 be regarded as a radical capable of replacing 1 eq. of hydrogen (similar to uranyl, U_2O_2, the hypothetical radical of the uranic salts), the formula of tartar-emetic dried at 212° may be written as $C_8H_4K(SbO_2)O_{12}$, and that of the salt dried between 392° and 428°, as $C_8H_2K(SbO_2)O_{10}$.

Antimonic acid, SbO_5, 160·24 *or* 2003.—This compound is obtained in the hydrated state: 1. By treating antimony with nitric acid, or with aqua-regia containing excess of nitric acid. 2. By decomposing pentachloride of antimony with water. 3. By precipitating a solution of antimoniate of potash with an acid.

The hydrated acid obtained by either of these methods gives off its water at a moderate heat, and yields *anhydrous antimonic acid* in the form of a yellowish powder, which is tasteless, insoluble in water, decomposes alkaline carbonates, and, when heated to redness, gives off oxygen, and is converted into antimoniate of antimonic oxide, $SbO_3.SbO_5$.

The hydrates obtained by the three methods above described are by no means identical. The acid in the first is monobasic, whereas in the other two it is bibasic. The bibasic acid is distinguished by the name of *metantimonic acid*, while the monobasic acid is called simply *antimonic acid* (Fremy).

Antimonic acid forms neutral or normal salts, containing $MO.SbO_5$, and acid salts whose formula is $MO.(SbO_5)_2$. Metantimonic acid forms neutral salts containing $(MO)_2.SbO_5$, and acid salts containing $(MO)_2.(SbO_5)_2$, or $MO.SbO_5$, so that the acid metantimoniates are isomeric or polymeric with the neutral antimoniates. An acid metantimoniate easily changes into a neutral antimoniate. The metantimoniates of potash, soda, and ammonia are crystalline; the antimoniates of the same bases are gelatinous and uncrystallizable. The soluble acid metantimoniates form a crystalline precipitate with salts of soda; the soluble antimoniates do not form any such precipitate (Fremy).

Antimoniates of potash.—The neutral salt, $KO.SbO_5.5HO$, is obtained by fusing 1 part of antimony with 4 parts of nitre, digesting the fused mass in tepid water to remove nitrate and nitrite of potash, and boiling the residue for an hour or two with water. The white insoluble mass of anhydrous antimoniate is thereby transformed into a hydrate containing 5 eq. water, which is soluble. The solution when evaporated leaves this hydrate in the form of a gummy uncrystallizable mass, which gives off 2 eq. of water at 320°, and the whole at a higher temperature.

Acid antimoniate of potash, $KO . (SbO_5)_2$ is obtained by passing carbonic acid gas through a solution of the neutral antimoniate. It is white, crystalline, perfectly insoluble in water, and is converted into the neutral salt when heated with excess of potash. This salt is the *antimonium diaphoreticum lavatum* of the pharmacopœias (Fremy).

Neutral metantimoniate of potash, $2KO.SbO_5$, is prepared by fusing antimonic acid or neutral antimoniate of potash with a large excess of potash. The fused mass dissolves in a small quantity of water, and the solution evaporated in vacuo yields crystals of the neutral metantimoniate. This salt dissolves freely and without decomposition in warm water containing excess of potash; but cold water or alcohol decomposes it into potash and the acid metantimoniate. Hence the aqueous solution of this salt gives a precipitate, after a while, with salts of soda (Fremy).

Acid metantimoniate of potash, $KO . SbO_5 + 7HO$, sometimes called *granular antimoniate of potash.*—This salt is used as a test for soda. To obtain it, the neutral antimoniate is first prepared and dissolved in the manner above described; the solution filtered to separate any acid antimoniate that may remain undissolved; then evaporated to a syrup in a silver vessel; and hydrate of potash added in lumps to convert the antimoniate into metantimoniate. The evaporation is continued till the liquid begins to crystallize, which is ascertained by taking out a drop now and then upon a glass rod, and the liquid is left to cool. A crystalline mass is thus obtained, consisting of neutral and acid metantimoniate of potash; the alkaline liquor is then decanted, and the salt dried upon filtering paper or unglazed porcelain (Fremy). This salt may also be prepared by treating terchloride of antimony with an excess of potash sufficient to redissolve the precipitate first formed, and adding permanganate of potash till the solution acquires a faint rose colour. The liquid, filtered and evaporated, yields crystals of the granular metantimoniate (Reynoso). This salt is sparingly soluble in cold water, but dissolves readily in water between 113° and 122°. When boiled with water for a few minutes, or kept in contact with water for some time, it is converted into the neutral antimoniate. It must therefore be preserved in the solid state, and dissolved just before it is required for use. A small quantity of it is then treated with about twice its weight of cold water to remove excess of potash, and convert any neutral metantimoniate into the acid salt; the liquid decanted; the remaining salt rapidly washed three or four times with cold water; then left in contact with water for a few minutes, and the liquid filtered. On adding to the solution thus obtained, a small quantity of any soda-salt, a crystalline precipitate is formed, consisting of *acid metantimoniate of soda*, $NaO . SbO_5 + 7HO$. This reaction is apparent in a solution containing only 1 part of soda in 300. In strong solutions of soda, the precipitate appears immediately, but in dilute solutions only after a while, the crystals being deposited on the sides of the vessel. An excess of potash in the reagent also retards the precipitation (Fremy*).

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* Traité de Chimie Générale, par Pelouze et Fremy, 2me. ed. t. 3, pp. 151, 157. According to Heffter (Pogg. Ann. lxxxvi. 418), the granular antimoniate of potash is $KO . HO + 12(KO . SbO_5 + 7HO)$; the precipitated soda-salt is similarly constituted; and by treating the solution of this salt in boiling water with salts of the earths and metallic oxides, precipitates are obtained, also of similar composition, or differing only in the water which they contain. Heffter's formulæ were calculated according to the old equivalent of antimony, 129; but Schneider has shown that, on re-calculating the analyses with the lower equivalent 120·24, the numbers of the equivalents of base and acid come out equal.

Antimoniates of ammonia.—When the metantimonic acid, obtained by decomposing pentachloride of antimony with water, is treated with ammonia, part of it dissolves, and a solution is formed containing *neutral metantimoniate of ammonia.* A few drops of alcohol added to the solution, throw down a precipitate consisting of *acid metantimoniate of ammonia,* $NH_4O . SbO_5 + 6HO$. This salt is slightly soluble, and its solution precipitates soda-salts. It changes spontaneously in a few days, even when kept in a close vessel, into neutral *antimoniate* of ammonia, which is completely insoluble in water. The same change is instantly produced in it by heat (Fremy).

Antimoniate of lead, $PbO . SbO_5$, may be obtained as a yellow powder by fusing antimonic acid with oxide of lead, or as a white hydrate by precipitation: the hydrate gives off its water when heated, and turns yellow. This salt is used as a pigment under the denomination of *Naples yellow.*

Antimoniate of antimony, $SbO_3 . SbO_5$. or SbO_4, is obtained by the action of heat upon antimonic acid, by roasting the teroxide or tersulphide, or by treating powdered antimony with excess of nitric acid. It is white, infusible, and unalterable by heat; slightly soluble in water. It was formerly regarded as a distinct acid, SbO_4, and called *antimonious acid;* but it does not form salts; and, when boiled with bitartrate of potash, it is resolved into cream of tartar, which dissolves, and a residue of antimonic acid.

Pentasulphide of antimony, Sulphantimonic acid, SbO_5, is obtained by passing hydrosulphuric acid gas into an acid solution of pentachloride of antimony, or into the solution of an alkaline antimoniate. It has an orange-colour much less red than the tersulphide; it is the *golden sulphuret of antimony* of several pharmacopœias. It combines with basic metallic sulphides, forming the *sulphantimoniates.* The *sodium-salt,* $3NaS . SbS_5$, which is sometimes used in medicine, is obtained by mixing 18 parts of finely-pounded tersulphide of antimony, 12 parts of dry carbonate of soda, 13 parts of lime, and 3¼ parts of sulphur; triturating the mixture for about half an hour; leaving it for two or three days in a flask filled with water, and shaking it from time to time; then filtering and evaporating, first over the open fire, afterwards in vacuo. The salt is thus obtained in large regular tetrahedrons of a pale yellow calour. It is very soluble in water, and is decomposed by acids, which throw down hydrated pentasulphide of antimony.

Pentachloride of antimony, $SbCl_5$, is obtained by heating metallic antimony in a current of dry chlorine, and distilling the product in a dry retort, rejecting the first portions of the distillate, which contain excess of chlorine. It is a yellowish, very volatile liquid, which emits suffocating vapours. Water first converts it into a crystalline hydrate, and then decomposes it, forming antimonic acid: $SbCl_5 + 5HO = SbO_5 + 5HCl$. It absorbs ammonia and phosphuretted hydrogen, forming red-brown solid compounds. It absorbs olefiant gas as readily as chlorine, and forms Dutch liquid. It likewise absorbs hydrosulphuric acid gas at ordinary temperatures, forming a white crystalline mass, consisting of *chlorosulphide of antimony,* $SbCl_3S_2$, exactly analogous to chlorosulphide of phosphorus, PCl_3S_2. Pentasulphide of antimony, treated with dry chlorine aided by heat, forms a white pulverulent compound, containing $SbCl_8S_3$, or $SbCl_5.3SCl$; this compound is decomposed at 572° (300° C.) into chlorine, chloride of sulphur, and terchloride of antimony. Pentachloride of antimony combines with hydrocyanic acid, forming a white, crystalline, volatile compound, composed of $SbCl_5.3HCy$. It also combines with chloride of cyanogen.

Antimoniuretted hydrogen.—This compound is obtained by dissolving an alloy of zinc and antimony in hydrochloric or dilute sulphuric acid, or by dissolving zinc in either of these dilute acids containing oxide or chloride of antimony, tartar emetic, &c. The gas, however, always contains more or less free hydrogen. Its comparative purity may be tested by means of a solution of nitrate of silver, which absorbs the antimoniuretted hydrogen, and leaves the free hydrogen. An alloy of 2 parts zinc and 1 part antimony yields the purest gas; an alloy containing a larger proportion of antimony gives more free hydrogen; and an alloy of equal parts of the two metals yields scarcely anything but free hydrogen. As the compound has never been obtained in a state of purity, its composition has not been correctly ascertained, but it is probably SbH_3.

Antimoniuretted hydrogen is a colourless gas, and when free from arsenic, quite inodorous. It is insoluble in water, and in alkaline liquids; with solutions of silver or mercury it forms precipitates containing silver or mercury, together with antimony. When burned from a jet, it deposits, on a plate of porcelain, metallic spots, greatly resembling those of arsenic, but differing from the latter in possessing less lustre and in not being soluble in hypochlorite of soda. They may also be dissolved in aqua-regia or in permanganate of potash (p. 540), and the solution will give the characteristic orange precipitate with hydrosulphuric acid. A metallic deposit may also be obtained by heating a glass tube through which the gas is passed; and this deposit, when sublimed, will not exhibit the characters of arsenic (p. 536).

Alloys of antimony with *potassium* or *sodium* may be obtained by igniting metallic antimony, or its oxide or sulphide, with an organic salt of potash or soda. Thus, when 5 parts of crude tartar and 4 parts of antimony are slowly heated in a covered crucible till the mixture becomes charred, then heated to whiteness for an hour, and left to cool, a crystalline regulus is obtained containing 12 per cent. of potassium. This alloy decomposes water rapidly, and oxidizes slowly in the air when in the compact state, but becomes heated and takes fire when rubbed to powder.

A mixture of 7 parts of antimony and 3 parts of *iron*, heated to whiteness in a crucible lined with charcoal, forms a white, very hard, slightly magnetic alloy, which gives sparks when filed. It is always formed when sulphide of antimony is reduced by iron in excess.

With *zinc*, antimony forms alloys of definite crystalline character. A fused mixture of the two metals, containing from 43 to 70 per cent. of zinc, deposits by partial cooling. silver-white rhombic prisms, containing from 43 to 64 per cent. of zinc. The alloy containing exactly 43 per cent. of zinc, appears to be a definite compound, *stibiotrizincyl*, $SbZn_3$. Mixtures containing from 33 to 20 per cent. of zinc deposit rhombic crystals containing from 35 to 21 per cent. of zinc. The alloy containing exactly 33 per cent. is *stibiobizincyl*, $SbZn_2$. These alloys, especially $SbZn_3$, decompose water with evolution of hydrogen at the boiling heat, and very rapidly under the influence of acids (J. P. Cooke*).

Type-metal, is an alloy of antimony and lead, usually containing 76 per cent. of lead, which corresponds nearly with the formula Pb_2Sb.

ESTIMATION OF ANTIMONY, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Antimony cannot be estimated in the form of antimonious or antimonic acid, because we can never be sure of the purity of those bodies. The best mode of proceeding is to precipitate it by hydrosulphuric acid, collect the sulphide of antimony on a weighed filter, and, after ascertaining the total quantity of the precipitate, estimate the proportion of sulphur in it in the manner already described with reference to sulphide of arsenic (p. 538). Or the sulphide of antimony may be decomposed by heating it in a current of hydrogen gas, whereupon hydrosulphuric acid and sulphur-vapour escape, and metallic antimony remains behind. For this purpose, a weighed portion of the sulphide is placed in a small porcelain crucible having a hole in its cover, through which a tube passes to convey the hydrogen. The temperature is gradually raised, and the process continued till the

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* Sill. Am. J. [2.] xviii. 229; xx. 222.

weight of the crucible no longer varies. The reduction may also be performed in a bulb-tube.

When antimonious and antimonic acids occur together in solution, the total quantity of antimony may be ascertained by treating one portion of the liquid in the manner just described, and the quantity existing as antimonious acid may be determined in another portion by means of terchloride of gold, 2 eq. of precipitated gold corresponding to 3 eq. of antimonious acid:

$$2AuCl_3 + 6HO + 3SbO_3 = 2Au + 6HCl + 3SbO_5.$$

The separation of antimony from the *alkalies* and *earths*, and from those metals which are not precipitated from their acid solutions by hydrosulphuric acid, is effected by means of that reagent.

To separate antimony from *cadmium*, *copper*, and *lead*, the solution, after being neutralized with ammonia, is mixed with sulphide of ammonium containing excess of sulphur. The sulphide of antimony then dissolves, the other sulphides remaining undissolved; and on mixing the filtrate with acetic acid (hydrochloric acid might redissolve a portion of the precipitate, especially as the liquid becomes heated), the sulphide of antimony is reprecipitated, and may be treated as above.

When antimony is combined with any of the preceding metals in the form of an alloy, it may be separated by treating the alloy with nitric acid, whereby the other metals are dissolved, and the antimony converted into insoluble antimonic acid. This method is, however, not rigidly exact; for the nitric acid dissolves a small portion of the antimony.

Separation of antimony from arsenic and tin.—The separation of these metals is attended with considerable difficulty. The best mode of effecting it is to convert them into arseniate, stannate, and antimoniate of soda, and treat the mixture with dilute alcohol, which dissolves the arseniate and stannate of soda, and leaves the antimoniate undissolved.

If the three metals exist together in solution, they must be precipitated as sulphides by hydrosulphuric acid, and the precipitate treated by one of the following methods:—

(1.) The precipitated sulphides are fused in a silver crucible with a mixture of hydrate of soda and nitre: or, better, they are oxidized by heating them with strong nitric acid; the solution, together with the insoluble stannic and antimonic acids, mixed with excess of caustic soda, and evaporated to a small bulk; then transferred to a silver crucible, evaporated to dryness, and kept for some time in a state of red hot fusion. The fused mass, consisting of arseniate, stannate, and antimoniate of soda, is disintegrated by digestion in warm water; the contents of the crucible transferred to a beaker-glass; and the crucible well rinsed out with a *measured* quantity of water. The greater part of the arseniate and stannate of soda then dissolves, while the antimoniate remains undissolved. But to effect complete separation, a quantity of alcohol of sp. gr. 0·833 is added, equal in bulk to one-third of the water used; the mixture left to stand for 24 hours and frequently stirred; and the antimoniate of soda, which has then completely settled down, is collected on a filter and washed, first, with a mixture of 1 volume of the same alcohol to 3 vols. of water, then with 1 vol. alcohol to 2 vols. water; next, with a mixture of equal measures of water and alcohol; and, lastly, with 3 vols. alcohol to 1 vol. water (H. Rose).*

(2.) The precipitated sulphides of the three metals are dissolved in a mixture of sulphide of sodium and caustic soda, and the liquid mixed with a solution of hypochlorite of soda. The sulphides are thereby oxidized and converted into arsenic, stannic, and antimonic acids, which combine with the soda, and may be separated by treatment with dilute alcohol, and washing, as in Rose's process. This method is due to Dr. Williamson; it is easier of execution than the former,

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* Handb. d. anal. Chem. 1851, ii. 429.

as the fused mixture of the soda-salts is very hard, and difficult to disintegrate by water.

The antimoniate of soda, separated by either of these processes, is digested in a mixture of hydrochloric and tartaric acids, which dissolves it completely; the antimony then precipitated by hydrosulphuric acid; and its quantity estimated in the manner already described (p. 545).

The filtrate containing the arseniate and stannate of soda is supersaturated with hydrochloric acid, which throws down a bulky precipitate of arseniate of stannic oxide; hydrosulphuric acid gas passed through the liquid till the white precipitate is completely converted into a brown mixture of the sulphides of tin and arsenic; the whole left to stand till the odour of hydrosulphuric acid is no longer perceptible; the precipitate collected on a weighed filter; and the filtrate heated for some time to expel the greater part of the alcohol; then mixed with sulphurous acid, and again treated with hydrosulphuric acid, whereby a small quantity of sulphide of arsenic is generally precipitated. This quantity of sulphide of arsenic being quite free from tin, need not be added to the mixed sulphides on the filter.

These mixed sulphides are dried at 212°, their total weight determined, and a known quantity heated in a stream of hydrosulphuric acid gas in the manner described at page 538. The residual sulphide of tin is then converted into stannic oxide, and the sublimed sulphide of arsenic, together with the small quantity separately precipitated, is converted into arsenic acid by treatment with hydrochloric acid and chlorate of potash, and the arsenic precipitated as ammonio-magnesian arseniate (H. Rose).

If the three metals are in the state of solid oxides, the mixture may be dissolved in hydrochloric acid, with addition of tartaric acid, and the metals precipitated as sulphides as before. If the metals are mixed in the form of an alloy, they may be dissolved in aqua-regia, the solution mixed with tartaric acid, then diluted, and precipitated in the same manner.

The method just described may, of course, be applied to the separation of antimony from tin or from arsenic alone. In these cases, however, simpler methods may often be advantageously adopted.

Separation of antimony from tin. — When these two metals exist together in solution, and the sum of their weights is known, the separation may be effected, and the weights of the two determined, by immersing in the solution a piece of pure tin, which precipitates the antimony in the form of a black powder. To render the precipitation complete, a gentle heat must be applied, and the solution must contain excess of acid. The antimony is collected on a weighed filter, dried at a gentle heat, and weighed. If the sum of the weights is not previously known, the metals must be precipitated together by zinc from a known quantity of the solution, and the antimony precipitated by tin from another portion. When the two metals exist together in an alloy, a portion of the alloy must be weighed, then dissolved in aqua-regia, and the solution mixed with tartaric acid, diluted with water, and treated as above.

Another method of separation is to precipitate the two metals with zinc, and treat the precipitate with strong hydrochloric acid without previously decanting the solution of chloride of zinc. The tin then dissolves, while the antimony remains undissolved, the presence of the chloride of zinc diminishing its tendency to dissolve in the acid. The tin may afterwards be precipitated by hydrosulphuric acid, and the sulphide converted into stannic oxide, by treating it with strong nitric acid (Levol).*

Separation of antimony from arsenic. — When these two metals are associated in the metallic state, they may be completely separated by heating the alloy in a stream of carbonic acid, the arsenic then volatilizing, and the antimony remaining

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* Ann. Ch. Phys. [3.] xiii. 125.

Antimony is, however, the only metal from which arsenic can be completely separated in this manner; hence, if the alloy contains any other metal, some of the arsenic will be retained, and the method is no longer applicable.

When this is the case, the alloy may be dissolved in aqua regia, or in hydrochloric acid to which chlorate of potash is gradually added; the solution diluted with water after addition of tartaric acid; then mixed with a considerable quantity of chloride of ammonium and excess of ammonia; and the arsenic precipitated as ammonio-magnesian arseniate by addition of sulphate of magnesia. The antimony may then be precipitated from the filtrate by hydrosulphuric acid.

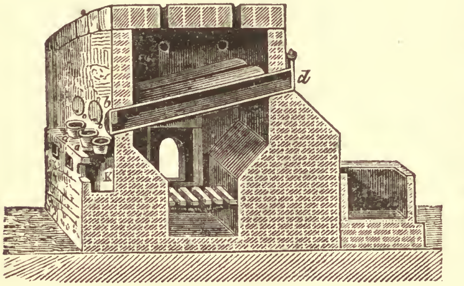
SECTION III.

BISMUTH.

Eq. 213, *or* 2662·5; Bi.

Bismuth is generally found in the metallic state, disseminated in quartz-rock; but occurs also as an oxide, carbonate, and sulphide, either alone or associated with other metals; also in combination with tellurium. Native bismuth is, however, the only mineral which occurs in sufficient abundance for the economical extraction of the metal. The process of extraction as performed in Saxony, whence all the bismuth of commerce is obtained, is very simple, the mineral being merely heated in close vessels, so as to melt the bismuth, and thereby separate it from the gangue or accompanying rock. The fusion is performed in iron tubes, laid in an inclined position, in a furnace. (Fig. 196.) The ore is introduced at the upper end, *d*, which is then plugged. The other end, *b*, is closed with an iron plate having an aperture, *o*, through which the melted metal runs into earthen pots, *a*, heated by a few coals placed in the space, *K*, below, so as to keep the metal in the melted state. It is then ladled out and run into moulds. The crude metal thus obtained is afterwards fused with 1-10th of its weight of nitre, to free it from sulphur, arsenic, and certain foreign metals.

Fig. 196.



Commercial bismuth, however, is still somewhat impure. To free it completely from other metals, it is dissolved in nitric acid, the clear liquid decanted and mixed with water, which throws down a subnitrate of bismuth; and this compound is reduced at a moderate heat, either with black flux, or in a crucible lined with charcoal.

Bismuth crystallizes in octohedrons and cubes. It may be obtained in very beautiful crystals, by fusing several pounds of the ordinary metal in a crucible or iron ladle, adding nitre from time to time, and stirring, till a portion of the fused metal, taken out and exposed to the air, no longer assumes an indigo colour, changing to violet or rose and disappearing on cooling, but a fine green or golden tint, which it retains on cooling; then leaving the metal to cool slowly, on a hot sand-bath, for instance, till a crust forms on the surface; piercing this crust with a hot coal; and pouring out the portion which still remains liquid. On subsequently detaching the crust, the inner surface of the metal is found to be covered with beautiful fretted cubes, like those of common salt.

Bismuth is moderately hard, slightly sonorous, and brittle, but may be somewhat extended by careful hammering. Its colour is reddish tin-white, with moderate lustre. The specific gravity of pure bismuth is 9·6542 (Karsten), 9·799 (Marchand and Scherer); of commercial bismuth, 9·822 (Brisson), 9·833 (Herapath), 9·861 (Bergman). Strong pressure rather diminishes than increases the density. Bismuth melts at 480° (Crichton); at 507° (Rudberg); at 509° (Hermann); and expands in solidifying. It boils at an incipient white heat, and if the air be excluded, sublimes in laminæ.

Bismuth forms four compounds with oxygen, viz., the bioxide, BiO_2; the teroxide, BiO_3; the quadroxide, BiO_4; and bismuthic acid, BiO_5.

Bioxide or *suboxide of bismuth.*—Bismuth oxidizes slowly when exposed to the air at ordinary temperatures, becoming covered with a brownish film of suboxide. When heated in the air till it fuses, it oxidates more rapidly, becoming covered with the same brown oxide, which is renewed as often as it is removed, till the whole of the metal is oxidized. This suboxide is also formed when subnitrate of bismuth is heated with protochloride of tin. By pouring a hydrochloric acid solution of equivalent quantities of teroxide of bismuth and protochloride of tin into excess of moderately strong potash, a black-brown precipitate is formed, consisting of a lower oxide of bismuth combined with stannic acid; and on treating this compound with stronger potash, the stannic acid dissolves and an oxide of bismuth remains, which, when dried in vacuo, or at 100°, out of contact with the air, forms a blackish-grey crystalline powder, consisting of BiO_2, retaining, however, a small quantity of water. It shows but little disposition to absorb oxygen at ordinary temperatures, but when heated, it is instantly converted, with a glimmering light, into teroxide. Acids decompose it into metallic bismuth and teroxide. When ignited in an atmosphere of carbonic acid, it becomes perfectly anhydrous, and in that state does not undergo any perceptible alteration by exposure to the air at ordinary temperatures, and oxidizes but slowly even at a red heat (R. Schneider).*

Teroxide of Bismuth, BiO_3; 237 or 3662·5.—Bismuth heated in the air till it boils, takes fire and burns with a faint bluish white flame, forming teroxide of bismuth, the vapour of which condenses on the surface of cold bodies in the form of *flowers of bismuth.* The same oxide is obtained in solution by acting on bismuth with nitric acid, the metal being then dissolved with evolution of nitrous fumes. Strong sulphuric acid likewise dissolves it at a boiling heat, with evolution of sulphurous acid. Hydrochloric acid acts but slightly on it, even with the aid of heat. When the solution of the nitrate is mixed with water, a white precipitate of subnitrate is produced; and this, when gently ignited, yields the teroxide in the form of a lemon-yellow powder. By fusing the hydrated oxide with hydrate of potash, or boiling it with potash-ley, the anhydrous oxide may be obtained in yellow shining needles. Teroxide of bismuth fuses at a strong red heat, and solidifies in a crystalline mass on cooling. It is easily reduced to the metallic state by potassium or sodium at a gentle heat, and by charcoal before the blowpipe.

Teroxide of bismuth combines with acids, forming salts which are very heavy, colourless, unless the acid itself is coloured, and exert a poisonous action. Heated on charcoal with carbonate of soda, they yield a button of metal. *Zinc, tin, cadmium, iron*, and *lead*, precipitate the metal from the solutions of these salts. *Water* decomposes most bismuth-salts — provided they do not contain too large an excess of acid, throwing down a sparingly soluble basic salt, while the acid remains in solution, together with a small quantity of oxide. *Hydrosulphuric acid* produces a brown-black precipitate of tersulphide of bismuth, insoluble in sulphide of ammonium. *Caustic alkalies*, at ordinary temperatures, throw down the white hydrated oxide, but at a boiling heat, especially if they are concentrated, they produce a yellow precipitate of the anhydrous oxide: these precipi-

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* Pogg. Ann. lxxxviii. 45.

tates are insoluble in excess of the alkali. *Alkaline carbonates* throw down a white precipitate of carbonate of bismuth, slightly soluble in excess, but precipitated from the solution by a caustic alkali. *Chromate* or *bichromate of potash* throws down a yellow chromate of bismuth, insoluble in caustic potash, whereby it is distinguished from chromate of lead. Sulphuric acid produces no precipitate.

Quadroxide of bismuth, BiO_4, — When a bismuth-salt contains free chlorine, caustic potash produces in it, not a white but a yellow precipitate, which consists of the hydrate of a higher oxide, but cannot be obtained free from chlorine. When this yellow hydrate is boiled with an alkaline chlorite having a strong alkaline reaction, it turns brown, like peroxide of lead, and is converted into the quadroxide of bismuth (Arppe). This oxide is completely dissolved by boiling nitric acid; any yellow or green residue that may be left, consists of bismuthic acid. It is perhaps a compound of teroxide of bismuth with bismuthic acid; $BiO_3.BiO_5$.

Bismuthic acid, BiO_5. — Prepared by passing chlorine through a strong solution of potash in which finely divided teroxide of bismuth is suspended; also, by heating a mixture of potash and teroxide of bismuth for a long time in contact with the air, — or better, by calcining a mixture of teroxide of bismuth, caustic potash, and chlorate of potash. Bismuthic acid, prepared by any of these methods, is always more or less mixed with teroxide of bismuth, which, however, may be dissolved out of weak nitric acid. Bismuthic acid is a light red powder, which, at a temperature a little above 212°, gives off part of its oxygen, and is converted into quadroxide of bismuth. Strong acids also decompose it, reducing it to the state of teroxide of bismuth, which then unites with the acid. Bismuthic acid combines with potash, and forms a few double salts, whose bases are the alkali and teroxide of bismuth.

Bisulphide of bismuth, BiS_2, separates in crystals from a fused mixture of metallic bismuth and the tersulphide, and may also be obtained by fusing 10 parts of bismuth with 3 parts of sulphur, melting the resulting mixture three times with fresh sulphur, and cooling quickly. Hydrochloric acid decomposes this compound, yielding metallic bismuth and the terchloride. Hence, and from the fact that its crystalline form is the same as that of the tersulphide, and that by fusing the tersulphide with metallic bismuth, in certain proportions, crystals may be obtained of the same form but containing less sulphur, Schneider concludes that the supposed bisulphide is merely a mixture of the tersulphide with metallic bismuth.

Tersulphide of bismuth, BiS_3, occurs native as *bismuth-glance*, and may be formed artificially by fusing bismuth with sulphur, and by decomposing bismuth-salts with hydrosulphuric acid. The native variety forms right rhombic prisms, isomorphous with sulphide of antimony: its colour is light lead-grey; specific gravity from 6·4 to 6·5. Tersulphide of bismuth is decomposed by heat; the native sulphide, heated in a tube, yields sublimed sulphur; and the artificial sulphide, when fused and left to cool, yields globules of metallic bismuth as it solidifies.

Selenide of bismuth, $BiSe_3$, is obtained by melting together 1 eq. of bismuth and 3 eq. of selenium, and re-melting the product with fresh selenium out of contact with the air. On a recently fractured surface, it exhibits a steel-grey colour, metallic lustre, and a distinct crystalline laminated texture. Its density is 6·82; hardness equal to that of galena; it may be readily pulverized. It is scarcely attacked by hydrochloric acid, but nitric acid and aqua regia decompose it readily (Schneider).

Bichloride of bismuth, $BiCl_2$, is formed by the action of dry hydrogen on the terchloride of bismuth and ammonium, $2NH_4Cl.BiCl_3$, at about 570°, or by heating 1 part of pulverized bismuth with 2 parts of subchloride of mercury in a sealed tube, at about 460°, and purifying the product by repeated fusion in sealed tubes. It is a black hygroscopic mass, which, by heating in the air, and by the action of acids, is resolved into metallic bismuth and the terchloride.

Terchloride of bismuth, $BiCl_3$. — Pulverized bismuth thrown into chlorine gas takes fire and burns with a pale blue light, forming the terchloride. This compound may also be obtained by heating 1 part of bismuth with 2 parts of protochloride of mercury, or by evaporating to dryness the solution of teroxide of bismuth in hydrochloric acid, and distilling the residue out of contact with the air. It is a white opaque solid, with a slight tinge of brown or grey, and a granular fracture; melts very readily, forming an oily liquid. The *hydrated terchloride* is obtained in crystals by dissolving the teroxide in hydrochloric acid, and evaporating. The anhydrous chloride, the crystals, and the solution are decomposed by water, yielding *oxychloride of bismuth*, $BiCl_3.2BiO_3$, in the form of an insoluble white powder, commonly known as *pearl-white*, — and hydrochloric acid holding a small quantity of bismuth in solution. A *sulphochloride*, of analogous composition, $BiCl_3.2BiS_3$, is obtained by heating chloride of bismuth and ammonium with sulphur or tersulphide of bismuth, or by passing hydrosulphuric acid gas over the same compound, heated to a temperature between 485° and 572°, and afterwards heating the product to its melting point in the same gas: —

$$3BiCl_3 + 6HS = BiCl_3.2BiS_3 + 6HCl.$$

The product of either of these operations, after being washed, first with water containing so much hydrochloric acid as not to give a precipitate with the terchloride, then with water slightly acidulated, and lastly with pure water, forms small, dark grey, crystalline needles, which, when heated in the air, give off, first, chloride of bismuth, then sulphurous acid, and leave a mixture of oxychloride and basic sulphate of bismuth (Schneider). A *seleniochloride*, $BiCl_3.2BiSe$, is obtained by adding terselenide of bismuth to fused chloride of bismuth and ammonium. It forms small needle-shaped crystals, having a dark steel-grey colour and metallic lustre (Schneider).

Terchloride of bismuth and ammonium.—A solution of 1 eq. of terchloride of bismuth and 2 eq. of sal-ammoniac, yields, by evaporation, double six-sided pyramids containing $2NH_4Cl.BiCl_3$, isomorphous with the corresponding terchloride of antimony and ammonium (Jacquelain). A solution of 1 eq. terchloride of bismuth and 6 eq. sal-ammoniac yields rhombic crystals, containing $3NH_4Cl.BiCl_3$ (Arppe).

Bismuth dissolves in a boiling solution of protochloride of copper, the liquid being decolorized, and appearing to contain the compound, $3Cu_2Cl . BiCl_3$. Bismuth dissolves in a similar manner in other cupric salts (Schneider).

Teriodide of bismuth, BiI_3 — Obtained as a crystalline sublimate by heating 1 eq. (32 parts) of tersulphide of bismuth with 3 eq. (475 parts) of iodine. Large, thin, crystalline laminæ, having the form of regular six-sided prisms, of a blackish grey colour, with a tinge of brown and a strong lustre. The compound, heated in the air, volatilizes for the most part, leaving a small quantity of basic oxide of bismuth of a red-brown colour. Boiling water converts it into the same compound. Aqueous potash decomposes it, forming iodate of bismuth, $BiO_3 . 3IO_3$: the same change is more slowly produced by alkaline carbonates. Alkaline sulphides decompose it, forming tersulphide of bismuth. Hydrochloric acid dissolves it without decomposition; nitric acid, with separation of iodine.

Sulphates of bismuth. — When bismuth is heated with strong sulphuric acid, sulphurous acid is evolved, and the metal is converted into a white insoluble powder, consisting of *tersulphate of bismuth*, $BiO_3 . 3SO_3$, which is decomposed by water, yielding a very acid salt which dissolves, and a *monobasic sulphate*, $BiO_3 . SO_3 + HO$, which remains. There is also a *bisulphate of bismuth*, which is obtained in small delicate needles when an acid solution of nitrate of bismuth is mixed with sulphuric acid (Heintz).

Carbonate of bismuth, $Bio_3 . CO_2$, is obtained by adding nitrate of bismuth to the solution of an alkaline carbonate: this salt is used in medicine.

Nitrates of bismuth. — The *neutral* or *ternitrate*, $BiO_3 . 3NO_5 + 10HO$, is obtained by dissolving bismuth in hot nitric acid, evaporating the solution, and leaving it to cool. The salt then separates in transparent oblique prisms of six or eight sides, and terminated with several faces. At 212° they separate into a solid and a liquid portion, the latter solidifying as it cools. At 302°, they are reduced to the mononitrate, $BiO_3 . NO_5 + HO$; which, when further heated to 500°, gives up all its acid and water, and leaves oxide of bismuth.

Subnitrates of bismuth. — *a.* Ternitrate of bismuth dissolves without decomposition in a small quantity of water, especially if a few drops of nitric acid are added. But a larger quantity of water decomposes it, forming a white precipitate of a subsalt, commonly called *magistery of bismuth.* This substance is generally regarded as a mononitrate containing one atom of water, $BiO_3 . NO_5 + HO$; but, according to Becker,* the basic nitrate obtained directly by treating the ternitrate with cold water, consists of $BiO_3 . NO_5 + 2\ HO$. This precipitate, when recently formed, dissolves somewhat freely in water, especially if the water contains nitric acid. Hence, if, after the precipitation of the basic salt, the supernatant liquid be mixed with a large quantity of water, the precipitate is completely redissolved; but after a while, a basic salt separates, containing $5BiO_3 . 4NO_5 + 9Aq$; this, according to Becker, is the true magistery of bismuth, inasmuch as, in the usual mode of preparing that substance, the same change takes place in washing the precipitate. Boiling water decomposes this salt, extracting all the nitric acid, excepting about 1 per cent. — *b.* A salt containing $5BiO_3 . 4NO_5 + 12HO$, is obtained by evaporating a solution of the ternitrate at a strong heat. When the precipitate first obtained by the action of cold water on a solution of the ternitrate is heated in contact with a free acid, or when the same acid solution is poured into hot water, a white, very loose powder is precipitated, containing $6BiO_3 . 5NO_5 + 9HO$. This salt is decomposed by water more readily than the preceding. If it be washed with water as long as the filtrate continues to exhibit a strong acid reaction, a crystalline residue is left on the filter, containing $4BiO_3 . 3NO_5 . 9Aq$. Duflos obtained a *magistery of bismuth* having the same composition, by treating the crystals of the neutral nitrate with 24 times their weight of water. Lastly, if the mononitrate, completely freed from the adhering acid liquid, be treated with water likewise free from acid, it dissolves completely; but the liquid after a while becomes milky, and after long standing deposits a white amorphous powder, containing $5BiO_3 . 3NO_5 + 8HO$. This salt may be formed, in addition to the true magistery of bismuth, if, in the preparation of that substance, too large a quantity of water be used, and the greater part of the acid liquid removed (Becker). Magistery of bismuth is used as a cosmetic, but has the serious disadvantage of being blackened by hydrosulphuric acid.

Bichromate of bismuth, $BiO_3 . 2CrO_3$. — When a solution of ternitrate of bismuth, containing as little free acid as possible, is poured into a moderately concentrated solution of bichromate of potash, bichromate of bismuth is obtained in the form of a yellow flocculent precipitate, which becomes dense and crystalline after a while, or immediately if heated. It may be dried without decomposition between 212° and 257°, but becomes blackish-green at a red heat. It contains 69·48 per cent. of teroxide of bismuth (J. Löwe).

The *alloys* of bismuth are remarkable for their fusibility. The amalgam of this metal is liquid. An alloy of 8 parts bismuth, 5 lead, and 3 tin, melts at 202°; another mixture of 2 bismuth, 1 lead, and 1 tin, at 200·75°: these mixtures are known by the name of *fusible metal.* Bismuth is also added to the alloy of tin and lead used for casting stereotype plates. Besides increased fusibility, bismuth communicates to this alloy the property of expanding on becoming solid, by which it is rendered capable of taking an accurate impression.

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* Archiv. Pharm. lv., 31 and 129.

ESTIMATION OF BISMUTH, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The best reagent for precipitating bismuth from its solutions is carbonate of ammonia; which, when added in excess, throws down the bismuth completely: the liquid must, however, be left to stand for some hours in a warm place, otherwise a considerable quantity of the bismuth will remain in solution. The precipitate, after being washed and dried, must be separated from the filter as completely as possible, the filter separately burned, and the precipitate ignited in a porcelain crucible: a platinum crucible would be attacked by it: after ignition, it consists of teroxide of bismuth containing 89·66 per cent. of the metal.

If the solution contains hydrochloric acid, the bismuth cannot be estimated by precipitation with carbonate of ammonia, or any other alkali, because the precipitate so produced would contain oxychloride of bismuth (p. 555). In this case, therefore, the bismuth must be precipitated by hydrosulphuric acid; the sulphide of bismuth oxidized and dissolved by nitric acid; and the diluted solution treated with carbonate of ammonia, as above.

Bismuth is separated from the *alkalies* and *earths*, and from *iron*, *cobalt*, *nickel*, *zinc*, and *chromium*, by hydrosulphuric acid; from *tin*, *arsenic*, and *antimony*, by sulphide of ammonium; from *lead*, by sulphuric acid; and from *copper* and *cadmium*, by ammonia. The separation of bismuth from cadmium may also be effected by cyanide of potassium, which dissolves the latter as cyanide of cadmium and potassium, and precipitates the bismuth. The precipitated bismuth, however, always contains potash, and must therefore be dissolved in nitric acid and precipitated by carbonate of ammonia. These two metals may also be separated by means of bichromate of potash, which throws down the bismuth as $BiO_3 . 2CrO_3$, and retains the cadmium in solution.

ORDER VII.

METALS NOT INCLUDED IN THE FOREGOING CLASSES, WHOSE OXIDES ARE NOT REDUCED BY HEAT ALONE.

SECTION I.

URANIUM.

Eq. 60 *or* 750; U.

THIS metal is obtained from *pitchblende*, a mineral containing from 40 to 95 per cent. of uranoso-uranic oxide, U_3O_4, associated with sulphur, arsenic, lead, iron, and several other metals. The mineral is finely pounded; freed by elutriation from the finer earthy impurities; roasted for a short time, to remove part of the sulphur and arsenic; then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water; the solution filtered from the brick-red residue of ferric oxide, ferric arseniate, and lead-sulphate; the greenish yellow filtrate slightly concentrated by evaporation, and left to cool, whereupon it deposits crystals; and the resulting radiated mass of crystallized uranic nitrate drained on a funnel, and then washed with a small quantity of cold water. As the water dissolves a portion of the crystals, it is used in a subsequent operation to redissolve the residue obtained by evaporating the solution of pitchblende in nitric acid. The uranic nitrate, after being dried in the air, is introduced into a wide-mouthed bottle containing ether, in which it immediately dissolves; the yellow solution is left to evaporate in the air; and the resulting crystals are purified by solution in hot water and recrystallization. The mixed mother-liquids, after dilution with water, are treated with hydrosulphuric acid to precipitate arsenic, lead, and copper, and the filtrate is freed from oxide of iron by evaporating to dryness and digesting the residue in water. The solution thus obtained yields a fresh crop of crystals of uranic nitrate. This salt is converted by ignition into uranoso-uranic oxide, U_3O_4, and from this the protoxide is obtained by ignition with reducing agents (Péligot).

Metallic uranium is obtained by decomposing the protochloride with potassium or sodium. If the mixture be heated in a platinum crucible over a spirit-lamp, and the soluble alkaline chloride washed out by water, the uranium is obtained in the form of a black powder, or sometimes aggregated on the sides of the crucible in small plates, having a silvery lustre and a certain degree of malleability. But, by introducing into a porcelain crucible, first, a layer of sodium, then chloride of potassium, and then a mixture of chloride of potassium and protochloride of uranium (the use of the chloride of potassium being to moderate the action, which is otherwise very violent), placing the porcelain crucible within a closed earthen crucible lined with charcoal, and heating it, first moderately, till the reduction takes place, and then strongly in a blast-furnace for 15 or 20 minutes, the metal is obtained in fused globules (Péligot).

Uranium, in its compact state, is somewhat malleable and hard, but is scratched by steel. Its specific gravity is 18·4; its colour is like that of nickel or iron. When exposed to the air, it soon tarnishes and assumes a yellowish colour. At a red heat it oxidizes with vivid incandescence, and becomes covered with a bulky layer of black oxide, which protects the interior from oxidation. In the pulverulent state, it takes fire at about 402°, burning with great splendour, and forming a dark-green oxide. It is permanent in the air at ordinary temperatures, and does not decompose cold water. It dissolves with evolution of hydrogen in dilute acids, forming green solutions. It combines directly with chlorine, giving out great light and heat, and forming a green volatile chloride. It unites directly with sulphur at a slightly elevated temperature (Péligot).

Uranium forms four compounds with oxygen, viz., the *protoxide*, UO; the *sesquioxide*, U_2O_3; and two intermediate oxides, U_4O_5, and, U_3O_4, which may be regarded as compounds of the other two, viz., $2UO.U_2O_3$ and $UO.U_2O_3$.

Protoxide of uranium; Uranous oxide, UO, 68, or 850. — This oxide is obtained by exposing uranoso-uranic oxide, mixed with charcoal powder, bullock's blood, or oil, to the strongest heat of a blast-furnace; by heating the same oxide to redness in a current of dry hydrogen; by igniting uranic oxalate out of contact of air, or better, in a current of hydrogen; or by igniting the chloride of uranyl and potassium (p. 556), either alone or in a current of hydrogen. Protoxide of uranium has sometimes the form of an earthy powder of a grey or brown colour; sometimes of crystalline scales having the metallic lustre. It was for a long time regarded as metallic uranium,* till Péligot † pointed out its true nature, and obtained the real metal in the manner above mentioned.

Uranous oxide, after ignition, is insoluble in boiling dilute hydrochloric or sulphuric acid, but dissolves in strong sulphuric acid. The hydrated oxide dissolves readily in acids. Solutions of uranous salts are green, and, when treated with alkalies or alkaline carbonates, or with carbonate of lime, yield a reddish-brown gelatinous hydrate of uranous oxide, which dissolves in alkaline carbonates, especially in carbonate of ammonia, forming a green solution. Alkaline hydrosulphates

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* See the first edition of this work, page 643.

† Ann. Ch. Phys. [3], v. 5; and xii. 258.

yield a black precipitate of uranous sulphide. Uranous salts are converted into uranic salts by exposure to the air, by the action of nitric acid, and by gold and silver salts; the action in the last case being accompanied by precipitation of metallic gold or silver.

Protochloride of uranium; Uranous chloride, UCl, is obtained by burning uranium in chlorine gas, or by passing that gas over an intimate mixture of charcoal and either of the oxides of uranium, strongly heated in a tube of very refractory glass. It crystallizes in dark-green regular octohedrons, which have a metallic lustre, and, when heated to redness, volatilize in red vapours and form a sublimate. It fumes strongly on exposure to the air, and dissolves very readily in water, forming a green solution.

Uranous sulphate, $UO.SO_3$, is found native as *uranium-vitriol,* and may be formed artificially by dissolving uranoso-uranic oxide in boiling oil of vitriol; or hydrated uranous oxide in dilute sulphuric acid; or by decomposing a concentrated solution of uranous chloride with sulphuric acid. Crystallizes with two and with four atoms of water. A *bibasic uranous sulphate* is obtained by treating the normal salt with a large quantity of water; by exposing the alcoholic solution of that salt to the sun's rays; by careful addition of ammonia to its aqueous solution; and by boiling that solution with green uranoso-uranic oxide. It forms a light-green powder having a silky lustre.

Uranoso-uranic oxide, U_3O_4, or $UO.U_2O_3$.—This oxide forms the principal constituent of pitchblende. It is obtained artificially by burning the metal or the protoxide in the air; by heating the protoxide to redness in an atmosphere of aqueous vapour; and by gentle ignition of uranic oxide or uranic nitrate. It is a dark-green powder which dissolves in acids, forming green solutions, exhibiting characters intermediate between those of uranous and uranic salts, and probably consisting of mere mixtures of the two.

Another intermediate oxide, U_4O_5, or $2UO.U_2O_3$, is said to be formed by strongly igniting the last oxide or the sesquioxide. It is black, and dissolves in acids, like the last; but it is probably a mere mixture of U_3O_4, with the protoxide.

Sesquioxide of uranium; Uranic oxide, U_2O_3; 144, *or* 1800.—Uranium and its lower oxides dissolve in nitric acid, with evolution of nitric oxide and formation of uranic nitrate. When a solution of this salt in absolute alcohol is evaporated at a gentle heat, till nitrous ether begins to escape, an orange-yellow spongy mass is obtained, consisting of hydrated uranic oxide mixed with undecomposed nitrate: the nitrate may be dissolved out by water, and the hydrated oxide then remains, exhibiting a lemon-yellow or orange-yellow colour. This hydrate is permanent in the air, and does not absorb carbonic acid. At 572°, it yields anhydrous uranic oxide, which is also yellow; and at a low red heat, it is converted into green uranoso-uranic oxide.

The *uranic* salts are obtained by oxidizing uranous or uranoso-uranic salts with nitric acid, or by exposing them to the air. Most of them contain one equivalent of uranic oxide combined with one equivalent of an acid. Now, as this is contrary to the usual analogy of the normal salts of sesquioxides, most of which contain three equivalents of acid to one equivalent of base, *e. g.*, ferric sulphate $= Fe_2O_3.3SO_3$; sulphate of alumina $= Al_2O_3.3SO_3$, — Péligot is of opinion that the base of these salts is not really a sesquioxide, but the protoxide of a compound radical, *uranyl,* U_2O_2, made up of the elements of 2 equivalents of uranous oxide: $U_2O_3{=}(U_2O_2)O$. To abbreviate the formulæ, we shall denote the compound radical, uranyl, by the symbol U'; we have then for the formula of uranic sulphate: $U_2O_3.SO_3 = (U_2O_2)O.SO_3 = U'O.SO_3$.

Uranic salts are yellow; they are mostly soluble in water, and, in solution, have a very rough taste, without any metallic after-taste. They are reduced to uranous salts by *hydrosulphuric acid;* also by *alcohol* or *ether,* in sunshine. *Caustic alkalies* added to uranic solutions throw down a yellow precipitate, consisting of a uranate of the alkali, which is insoluble in excess of the reagent. *Alkaline carbonates* produce a yellow precipitate, consisting of a carbonate of uranic oxide and the alkali, soluble in excess, especially in bicarbonate of potash or sesquicarbonate of ammonia. Potash added to these solutions throws down all the uranic oxide. From the solution in carbonate of ammonia, the uranic oxide is likewise precipitated by boiling. *Carbonate of baryta* precipitates uranic oxide completely from its solutions at ordinary temperatures. *Phosphate of soda,* added to uranic salts not containing too much free acid, produces a white precipitate of uranic phosphate, having a slight tinge of yellow. *Sulphide of ammonium* produces a black precipitate of uranic sulphide, which remains for a long time suspended in the liquid. *Hydrosulphuric acid* produces no precipitate. *Ferrocyanide of potassium* produces a dark red-brown precipitate; *ferricyanide of potassium,* none. Metallic *zinc* does not precipitate uranium in the metallic state from uranic solutions, but, after a long time, produces a yellow precipitate of uranic oxide.

Uranic oxide and its salts, fused with *phosphorus-salt* in the outer blowpipe flame, produce a clear yellow glass which becomes greenish on cooling. In the inner flame, the glass assumes a green colour, becoming still greener when cold. Similar colours with *borax.* The oxides of uranium are not reduced to the metallic state by fusion with carbonate of soda on charcoal. Uranic oxide is used for imparting a delicate yellow tint to glass; the glass thus coloured is called *canary glass.*

Chloride of uranyl, $U_3O_3Cl = U'Cl$) — When dry chlorine gas is passed over uranous oxide at a red heat, the tube becomes filled with an orange-yellow vapour of this compound, which solidifies in a yellow crystalline mass, easily fusible, but not very volatile. Dissolved in water, it forms hydrated chloride of uranyl, or hydrochlorate of uranic oxide:

$$U_2O_2Cl + HO = U_2O_3.HCl.$$

Chloride of uranyl and potassium, $KCl.UCl + 2Aq.$, is formed by evaporating an aqueous mixture of uranic chloride and chloride of potassium. By heating the hydrated crystals to 212°, the anyhdrous compound is obtained.

Uranic sulphate; sulphate of uranyl. — The monosulphate $V'O.SO_3 + 3Aq.$ is obtained by dissolving uranoso-uranic oxide in strong sulphuric acid, diluting the solution with water, and oxidizing with nitric acid; also by decomposing a solution of uranic nitrate with sulphuric acid, expelling the excess of acid by heat, dissolving the residue in water, evaporating the solution to a syrup, and leaving it to crystallize. Forms small lemon-yellow prisms. According to Berzelius, a *bisulphate* and a *tersulphate* are obtained by dissolving the monosulphate in sulphuric acid; but Péligot denies their existence. A basic sulphate is found native in the form of a yellow powder. The monosulphate forms, with sulphate of potash, a crystalline double salt, whose formula is:

$$KO.SO_3 + U_2O_3.SO_3 + 2HO = \left.\begin{matrix}K\\U'\end{matrix}\right\} 2SO_4 + 2HO.$$

Uranic nitrate; nitrate of uranyl; $U_2O_3.NO_5 = U'O.NO_5$, is formed by treating the metal or either of its oxides with nitric acid. It crystallizes in lemon-yellow prisms. The solution of this salt possesses the power of lowering the refrangibility of rays of light which fall upon it, producing the peculiar phenomenon called *fluorescence.* This property is likewise exhibited by other compounds of uranium, especially by *canary-glass.* A *basic* nitrate is formed by gently igniting the normal salt.

Uranic phosphates; phosphates of uranyl. — Three of these salts are known, all containing 3 atoms of base to 1 atom of acid. When uranic oxide is digested in a small quantity of aqueous phosphoric acid, a yellow saline mass is produced, part of which dissolves in boiling water, leaving a light yellow powder, which is the *neutral phosphate* $(2U'O.HO).PO_5$. The aqueous solution concentrated by heat, and then left to evaporate in vacuo over oil of vitriol, deposits a lemon-yellow crystalline salt, consisting of the *acid phosphate*, $(U'O.2HO).PO_5$. The *basic phosphate* has not been obtained in the separate state; but when uranic nitrate is mixed with a moderate excess of basic phosphate of soda $(3NaO.PO_5)$, a dark yellow precipitate is formed, containing $(NaO.2U'O).PO_5+3U'O.PO_5$ (Wertheim).* When uranic acetate is added to a solution of any soluble phosphate containing an abundance of ammonia and free acetic acid, a yellow precipitate is formed consisting of *ammonio-uranic phosphate*, $2U'O.NH_4O.PO_5$, which, when ignited, leaves uranic pyrophosphate, $2U'O.PO_5$. This reaction affords a ready and exact method of estimating phosphoric acid. The insoluble phosphates, even those of alumina and sesquioxide of iron, are also decomposed by boiling with uranic acetate in presence of a large excess of acetate of ammonia and free acetic acid, the bases dissolving, while the phosphoric remains undissolved in the form of the ammonio-uranic phosphate above described. To separate phosphoric acid from iron in this manner requires, however, a very large excess of the uranium salt (W. Knop).†

A neutral and an acid *arseniate of uranyl*, analogous in composition to the phosphates, have also been obtained by similar means. The composition of these phosphates and arseniates affords a strong argument in favour of the uranyl theory.

Compounds of uranic oxide with bases.—Uranic oxide combines as an acid with the alkalies, earths, and other metallic oxides, forming salts which may be called *uranates*. The uranates of the alkalies are obtained by precipitating a solution of uranic oxide in an acid with an alkali; the uranates of the earths and heavy metallic oxides, by adding ammonia to a solution of an uranic salt mixed with one of these bases. The uranates are for the most part yellow, and after ignition orange-yellow. The soda-compound, $NaO.2U_2O_3+6HO$, is used for colouring glass, and is prepared on the large scale by roasting pitchblende with limestone in a reverberatory furnace; treating the resulting uranate of lime with dilute sulphuric acid, by which the uranic oxide is almost completely dissolved; mixing the green solution with crude carbonate of soda, by which the uranium is precipitated together with other metals, but redissolved tolerably free from impurities by excess of the alkali; and treating the liquid with dilute sulphuric acid as long as effervescence is produced. The uranate of soda is then precipitated in a form well adapted for the manufacture of yellow glass.

ESTIMATION OF URANIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Uranium is completely precipitated from uranic solutions by ammonia. The precipitate, which consists of hydrated uranic oxide containing ammonia, must be washed with water containing sal-ammoniac, as it runs through the filter when washed with pure water. It is then dried and ignited in an open crucible, whereby it is converted into uranoso-uranic oxide, U_3O_4; but to obtain a perfectly definite result, and prevent further oxidation during cooling, it is necessary to put the cover on the crucible while the substance is still red-hot, and keep it there till the crucible is quite cold. The oxide thus obtained contains 84·90 per cent. of uranium. An accurate result is likewise obtained by igniting the sesquioxide in an atmosphere of hydrogen, whereby it is reduced to protoxide containing 88·24 per cent. of the metal.

If the uranic solution contains a considerable quantity of an earth or a fixed alkali, the precipitate formed by ammonia carries down with it a certain portion of the earth or alkali; to free it from which it must, before ignition, be redissolved in hydrochloric acid and reprecipitated by ammonia.

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* J. pr. Chem. xliii. 321.

† Chem. Gaz. 1856, 467.

From the *fixed alkalies*, uranium, in the state of sesquioxide, is separated by ammonia, attention being paid to the precaution just mentioned.

From *baryta* it is separated by sulphuric acid; from *strontia* and *lime*, also by sulphuric acid with addition of alcohol.

From *magnesia*, *manganese*, *cobalt*, *nickel*, and *zinc*, these metals being in the state of protoxide, and the uranium in the state of sesquioxide, it is separated by precipitation with carbonate of baryta.

From *iron* it is separated by carbonate of ammonia, both metals being in the state of sesquioxide; the uranic oxide then dissolves, while the ferric oxide remains undissolved. Care must, however, be taken that the carbonate of ammonia be really monocarbonate, quite free from excess of carbonic acid, otherwise the iron will also be dissolved. To ensure this condition, the carbonate of ammonia must be previously boiled, and the solution of the oxides, if acid, must be neutralized with ammonia till a slight permanent precipitate begins to form: the solution should then be diluted with water. The uranic oxide is separated from the filtrate either by boiling, or by supersaturation with hydrochloric acid and precipitation by ammonia.

From *alumina*, uranium is also separated by carbonate of ammonia, and with greater facility.

From *cadmium*, *copper*, *lead*, *tin*, *arsenic*, *antimony*, and *bismuth*, uranium is separated by hydrosulphuric acid; from *titanium* and *chromium* in the same manner as iron is separated from those metals (pp. 505, 514); and from *vanadium*, *tungsten*, *molybdenum*, and *tellurium*, by sulphide of ammonium, in which the sulphides of the last named metals are soluble.

SECTION II.

CERIUM.

Eq. 47·26, *or* 590·87. Ce.

This metal, which was discovered in 1803, simultaneously by Klaproth, and by Hisinger and Berzelius, exists, together with lanthanum and didymium, in cerite, allanite, orthite, yttro-cerite, and a few other minerals, all of somewhat rare occurrence. The most abundant of them is cerite, which is a compound of silicic acid with the oxides of cerium, lanthanum, and didymium, together with small quantities of lime and oxide of iron. To extract the oxides of the three metals, the cerite is finely pounded and boiled for some hours with strong hydrochloric acid, or aqua-regia, which dissolves the metallic oxides, leaving nothing but silica. The filtered solution is then treated with a slight excess of ammonia, which precipitates everything but the lime; the precipitate is redissolved in hydrochloric acid, and the solution treated with excess of oxalic acid. A white or faintly rose-coloured precipitate is then obtained, consisting of the oxalates of cerium, lanthanum, and didymium: it is curdy at first, but in a few minutes becomes crystalline, and easily settles down. When dried and ignited, it yields a red-brown powder, containing the three metals in the state of oxide. The finely pounded cerite may also be mixed with strong sulphuric acid to the consistence of a thick paste, the mixture gently heated till it is converted into a dry white powder, and this powder heated somewhat below redness in an earthen crucible. The three metals are thus brought to the state of basic sulphates, which dissolve completely when very gradually added to cold water; and the solution treated with oxalic acid yields a precipitate of the mixed oxalates, which may be ignited as before.

From the red-brown mixture of the oxides of cerium, lanthanum, and didymium thus obtained, a pure oxide of cerium may be prepared by either of the following processes: — 1. The mixed oxides are heated with strong hydrochloric acid, which dissolves the whole, with evolution of chlorine; the solution precipitated with excess of caustic potash: and chlorine gas passed through the liquid with the precipitate suspended in it. The cerium is thereby brought to the state of sesquioxide, which is left undissolved in the form of a bright yellow precipitate, while the lanthanum and didymium remain in the state of protoxides, and dissolve. To ensure complete separation, the passage of the chlorine must be continued till the liquid is completely saturated with it, and the solution, together with the precipitate, left for several hours in a stoppered bottle, and agitated now and then. The liquid is then filtered, the washed precipitate treated with strong boiling hydrochloric acid, which dissolves it with evolution of chlorine, and forms a colourless solution of protochloride of cerium; and this, when treated with oxalic acid or oxalate of ammonia, yields a perfectly white precipitate of oxalate of cerium, which may be converted into oxide by ignition (Mosander). 2. The red-brown mixture of the three oxides is treated with very dilute nitric acid (1 part of nitric acid of ordinary strength to between 50 and 100 parts of water), which dissolves the greater part of the oxides of lanthanum and didymium, and leaves the oxide of cerium; and by treating the residue with very strong nitric acid, the last traces of lanthanum and didymium may be extracted (Mosander, Marignac). 3. The red-brown mixture of the three oxides is boiled for several hours in a strong solution of chloride of ammonium. The oxides of lanthanum and didymium then dissolve, with evolution of ammonia, and ceric or ceroso-ceric oxide is left in a state of purity. It must be collected on a filter and washed with a solution of sal-ammoniac, because, when washed with pure water, it first runs through the filter, and then stops it up (Watts).*

Metallic cerium is obtained by heating the pure anhydrous protochloride with potassium or sodium. It is a grey powder which acquires the metallic lustre by pressure. It oxidizes readily, decomposes water slowly at ordinary temperatures, quickly at the boiling heat, and dissolves rapidly in dilute acids, with evolution of hydrogen, forming a solution of a cerous salt.

Protoxide of cerium; Cerous oxide, CeO; 55·26 or 690.8. — This oxide is scarcely known in the anhydrous state. The sesquioxide, exposed to the strongest heat of a wind-furnace, in a crucible lined with charcoal, yields a residue chiefly consisting of protoxide, but the reduction is never complete. The hydrated protoxide is easily obtained by precipitating the chloride with a caustic alkali. It dissolves readily in acids, forming the *protosalts of cerium* or *cerous salts*, the solutions of which are distinguished by the following characters: *Caustic potash* or *soda* produces a white precipitate of the hydrated protoxide, which is insoluble in excess, and is converted into the yellow sesquioxide by the action of chlorine or hypochlorous acid. *Ammonia* precipitates a basic salt. *Alkaline carbonates* form a white precipitate of cerous carbonate insoluble in excess. *Oxalic acid* or *oxalate of ammonia* produces a white precipitate of cerous oxalate, gelatinous at first, but quickly assuming the crystalline character, and converted by ignition in an open vessel into a salmon-coloured powder, consisting of sesquioxide of cerium mixed with protoxide. Hydrosulphuric acid produces no precipitate. *Sulphide of ammonium* throws down the hydrated protoxide. *Ferrocyanide of potassium* produces a white pulverulent precipitate; ferricyanide of potassium, none. *Sulphate of potash* produces a white crystalline precipitate of potassio-cerous sulphate, nearly insoluble in pure water, and quite insoluble in excess of sulphate of potash. With dilute solutions the precipitate takes some time to form. This character, together with the behaviour of the oxalate, and the yellow coloration of the hydrated protoxide by chlorine, serves to distinguish cerium from all other metals. Cerous salts in solution have a sweet astringent taste, and redden litmus, even when the acid is perfectly saturated. All compounds of cerium, ignited with

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* Chem. Soc. Qu. J. ii. 147.

borax or *phosphorus-salt* in the outer blowpipe-flame, yield a glass which is deep red while hot, but becomes colourless on cooling. In the inner flame a colourless bead is formed, but when ignited with excess of oxide of cerium, it forms a yellow enamel.

Sesquioxide of cerium; Ceric oxide, Ce_2O_3.—It is doubtful whether this oxide has been obtained in the separate state. The hydrated protoxide, the nitrate, and the oxalate, yield, when ignited in the acid, a salmon-coloured powder, which is generally regarded as ceric oxide; but, according to Marignac, it is a mixture or compound of the sesquioxide and protoxide of cerium, not quite constant in composition, but containing on the average 82·15 per cent of metal, and therefore nearly agreeing with the formula Ce_7O_9 or $3CeO.2Ce_2O_3$. When mixed with oxide of didymium, its colour is red-brown. This oxide is nearly insoluble in strong nitric and hydrochloric acids, even at the boiling heat, but strong boiling sulphuric acid dissolves it. Hydrochloric acid, with the aid of reducing agents, such as alcohol, dissolves it slowly at the boiling heat, forming a solution of cerous chloride. If mixed with the oxide of lanthanum or didymium, it dissolves readily in strong boiling hydrochloric acid, with evolution of chlorine. The solution of this oxide in strong sulphuric acid has a bright yellow colour, and deposits yellow prismatic crystals, which, according to Marignac, consist of a *ceroso-cericsulphate*, containing $Ce_7O_9 . 4SO_3 + 7HO$. Potash, added to the solution of this salt, throws down a yellow hydrate, which dissolves readily in acids. The solutions are yellow, and, when boiled with hydrochloric acid, are converted into cerous salts.

Protosulphide of cerium, CeS, is obtained by igniting the carbonate in vapour of bisulphide of carbon, or by heating an oxide of cerium with sulphide of potassium. The first process yields a light powder of the colour of red lead; the second, a product resembling mosaic gold. The *sesquisulphide of cerium* is not known in the free state, but exists in certain sulphur-salts.

Protochloride of cerium, CeCl.—Cerium burns vividly when heated in chlorine gas, and forms this compound. The anhydrous chloride may be prepared by igniting the sulphide, or the residue obtained by evaporating to dryness a solution of the chloride mixed with sal-ammoniac, in a current of chlorine gas. If the air is not completely excluded, an oxychloride is also produced. The anhydrous chloride is a white porous mass, fusible at a red heat, and perfectly soluble in water. A *hydrated chloride* is obtained in colourless four-sided prisms, by dissolving the hydrated oxide or the carbonate in hydrochloric acid, and evaporating to a syrup. The solution, when exposed to the air, turns yellow, from formation of a ceric salt..

Sesquichloride of cerium.—The hydrated sesquioxide dissolves in cold hydrochloric acid, forming a red solution, which, however, soon gives off chlorine, and is reduced, more or less completely, to protochloride.

Protofluoride of cerium is formed by precipitating the protochloride with an alkaline fluoride. The *sesquifluoride* occurs native in six-sided prisms, mixed with half its weight of protofluoride; also with the fluorides of yttrium and calcium, in *yttrocerite*. An oxyfluoride of cerium, $Ce_4F_3O_3 + 3HO$, is also found native.

Cerous carbonate, $CeO . CO_2 + 3HO$, is formed by exposing the hydrated protoxide to the air, or by precipitation.

Cerous oxalate, $C_4Ce_2O_8$, is precipitated from cerous salts by oxalic acid or oxalate of ammonia added in excess, even when the solution contains a considerable quantity of free nitric or hydrochloric acid. It is at first curdy, but soon becomes very dense and crystalline. When ignited with free access of air, it yields ceroso-ceric oxide.

Cerous sulphate, $CeO . SO_3$.—The anhydrous salt is a white powder, which, when sprinkled with a small quantity of water, becomes very hot, and condenses into a solid mass, very difficult to dissolve. It forms two crystalline hydrates, viz., $2(CeO . SO_3) + 3HO$ and $(CeO . SO_3) + 3HO$. The anhydrous salt, heated in a close vessel, leaves a basic cerous sulphate; but, with free contact of air, it leaves a basic ceric or ceroso-ceric sulphate. Cerous sulphate forms with sulphate of potash a crystalline double salt, containing $CeO.SO_3+KO.SO_3$, which is nearly insoluble in water.

Cerous phosphate.—Obtained by precipitating a cerous salt with phosphate of soda. It also occurs native (associated with the phosphates of lanthanum and didymium), in several forms. In *Monazite* and *Edwardsite*, it occurs in oblique rhombic prisms; in the former it is associated with thorina, and small quantities of lime, manganese, and tin; in the latter, with alumina, zirconia, and silica. *Cryptolite* is a tribasic phosphate of cerium, occurring in rose-coloured apatite of Arendal in Norway, and is separated by dissolving the apatite in nitric acid. It then remains in the form of a crystalline powder, appearing under the microscope to consist of hexagonal prisms. Sp. gr. 4·6 (Wöhler).* *Phosphocerite* is a mineral similar in composition to cryptolite. It was discovered by Mr. O. Sims in the cobalt-ore of Johannisberg in Sweden, of which it forms about one-thousandth part. It remains as a residual product when the ore after calcination is treated with hydrochloric acid for the purpose of extracting the cobalt. It is a greyish yellow crystalline powder, mixed with a small quantity of minute dark purple crystals, which are strongly attracted by the magnet, and consist chiefly of magnetic oxide of iron. The crystals of phosphocerite, when examined by the microscope, exhibits two forms, one an octohedron, the other, a four-sided prism with quadrilateral summits, both forms apparently belonging to the right prismatic system. Sp. gr. 4·78. The mineral contains 64·68 per cent. protoxide of cerium, &c., 28·46 phosphoric acid, 2·83 oxide of iron, and 3·41 oxide of cobalt, silica, &c. It is very rich in didymium. Strong sulphuric acid, aided by gentle heat, decomposes it, forming a pasty mass, which dissolves in cold water with the exception of a small quantity of silica (Watts).†

ESTIMATION OF CERIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Cerium is precipitated from neutral solutions of cerous salts by potash, as cerous hydrate; or by oxalate of ammonia, as cerous oxalate; and either of these compounds is converted by ignition in an open vessel into ceroso-ceric oxide. This oxide, as already observed, is not perfectly definite in constitution; it may be stated approximately to contain 96·5 per cent. of cerous oxide, or 82·5 per cent. of the metal, and this estimate may be adopted where great accuracy is not required. A more exact method, however, is to dissolve the hydrate precipitated by potash in dilute sulphuric acid, then evaporate, and heat the residue to commencing redness, whereby it is converted into the anhydrous sulphate $CeO.SO_3$, containing 57·6 per cent. of the protoxide of cerium, or 49·6 per cent. of the metal.

Hydrosulphuric acid serves to separate cerium from all metals which are precipitated by that reagent from their acid solutions.

From *manganese*, *iron*, *cobalt*, *nickel*, *zinc*, *titanium*, *chromium*, *vanadium*, and *tugsten*, cerium may be separated by means of a saturated solution of sulphate of potash.

From *alumina* it may be separated by carbonate of baryta, which precipitates alumina and not cerous oxide; from *glucina* by sulphate of potash.

From *yttria*, with which it is often associated in minerals, it is separated by a saturated solution of sulphate of potash added in excess, the sulphate of yttria and potash being soluble in excess of sulphate of potash, while the cerous double salt remains undissolved.

From *zirconia*, cerium is separated by treating the boiling acid solution with sulphate of potash, whereby the greater part of the zirconia is precipitated as basic sulphate, while the cerium remains dissolved; to complete the precipitation,

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* Ann. Ch. Pharm. lvii., 268.

† Chem. Soc. Qu. J. ii. 131.

a small quantity of ammonia must be added, but not sufficient to saturate the acid (H. Rose).

From *magnesia* also cerium may be separated by sulphate of potash; from *baryta*, *strontia*, and *lime*, it is separated by ammonia added in slight excess; or from baryta by sulphuric acid, and from strontia and lime by sulphuric acid and alcohol; and from the *fixed alkalies* by precipitation with oxalate of ammonia.

SECTION VI.

LANTHANUM.

Eq. 27 *or* 588; La.

The red-brown oxide obtained from cerite by the methods already described (p. 558), and originally regarded as the oxide of a single metal, cerium, was shown by Mosander,* in 1839, to contain the oxide of another metal, to which he gave the name *lanthanum.* Subsequently, in 1841,† Mosander discovered that even this supposed simple oxide contained two distinct metals, for one of which the name of lanthanum was retained, while the other was called *didymium.* These two metals appear to be constantly associated with cerium, though not always in the same proportion.

The separation of lanthanum and didymium from cerium may be effected by either of the methods already described (p. 559); the second and third are easier and more expeditious than the first. If the solution obtained by treating the crude red-brown oxide with dilute nitric acid be evaporated to dryness, and the residue treated with nitric acid diluted with at least 200 parts of water, a solution will be obtained quite free from cerium (Marignac). Boiling the red-brown oxide with chloride of ammonium also yields a solution of lanthanum and didymium free from cerium. In both cases, however, it is best to test a portion of the solution for cerium by precipitating with excess of caustic potash, and passing chlorine through the solution. The presence of cerium, even in very small quantity, will be indicated by the formation of a yellow precipitate, after the liquid, supersaturated with chlorine, has been left in a close vessel for several hours.

A solution free from cerium having been obtained, the separation of the lanthanum and didymium is effected by the different solubilities of their sulphates. To convert them into sulphates, the solution is treated with excess of a caustic alkali, and the washed precipitate dissolved in dilute sulphuric acid. The mode of proceeding varies according as the lanthanum or the didymium is in excess.

1. When the lanthanum is in excess, in which case the solution has but a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated in a platinum-dish to a temperature just below redness, to drive off the excess of acid, and render the sulphates perfectly anhydrous. The residue is then dissolved in rather less than six times its weight of water, at about 36° Fah. (2° or 3° C.), the salt being reduced to powder and added in successive small portions, and the vessel containing the liquid being immersed in ice-cold water. Without these precautions, the temperature of the liquid may be raised several degrees, in consequence of the heat evolved by the combination of the anhydrous sulphates with water; and, in that case, crystallization will commence, and rapidly extend through the whole mass of liquid, as these sulphates are much less soluble in warm than in cold water; but if the liquid be properly cooled, the whole dissolves completely. The solution is next to be heated in the water-bath to about 104° F. (40° C.); the sulphate of lanthanum then crystallizes out, accompanied by only a small quantity of sulphate of didymium. To purify it completely, it is again rendered anhydrous, re-dissolved in ice-cold water, &c., and the entire process repeated ten or

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[*] Pogg. Ann. xlvi. 648; xlvii. 207.

[†] Ibid. lvi. 504.

twelve times. The test of purity is perfect whiteness, the smallest quantity of didymium imparting an amethyst tinge (Mosander).

2. When the didymium-salt is in excess, in which case the liquid has a decided rose-colour, separation may be effected by leaving the solution containing excess of acid, in a warm place for a day or two. The sulphate of didymium then separates in large rhombohedral crystals modified with numerous secondary faces; and, at the same time, slender, needle-shaped, violet-coloured crystals are formed, containing the two sulphates mixed. The rhombohedral crystals, which are nearly free from lanthanum, are removed, and the needles, together with the mother-liquid, treated as in the first method, to obtain sulphate of lanthanum (Mosander).

In both cases, the separation may be greatly facilitated by first dissolving the mixed oxides of the two metals in a large excess of nitric acid, and precipitating in successive portions by oxalic acid: the first precipitates thus formed have a much deeper rose-colour, and are much richer in didymium than the latter. The separation thus effected is very imperfect in itself, but it greatly facilitates the subsequent separation of the sulphates, which is much more rapid, when one of the sulphates is in great excess with regard to the other (Marignac).

Metallic lanthanum is obtained by decomposing the anhydrous chloride with sodium, and dissolving out the chloride of sodium with alcohol of sp. gr. 0·833. It is a dark, lead-grey powder, soft to the touch, and adhering when pressed.

Protoxide of lanthanum, LaO, 55 or 688, is obtained in the anhydrous state by igniting the precipitated hydrate or carbonate in a covered crucible. It is a white powder, which turns brown when heated in the air, probably from partial conversion into a higher oxide. The *hydrated oxide* is formed when the metal or the anhydrous oxide is immersed in warm water, or when a salt of lanthanum is precipitated by caustic potash. It is a white substance, viscid while moist, and slightly alkaline to test-paper. It absorbs carbonic acid from the air with great rapidity.

Oxide of lanthanum, even after strong ignition, dissolves very easily in acids. When boiled with a solution of chloride of ammonium, it dissolves and expels the ammonia. The salts of lanthanum are perfectly colourless when free from didymium. The soluble salts have an astringent taste. *Potash* and *soda*, added to the solutions, throw down the hydrated oxide, which dissolves completely in chlorine-water, without forming any yellow deposit. *Ammonia* throws down a basic salt. *Oxalic acid* or *oxalate of ammonia*, throws down a white flocculent precipitate, which does not become crystalline. In other respects, the solutions resemble those of cerous salts. Compounds of lanthanum do not impart any colour to borax or phosphorus salt.

Chloride of lanthanum is obtained in the anhydrous state by igniting the oxide in a current of hydrochloric acid gas, and as a hydrate by evaporating a solution of the oxide in hydrochloric acid. It dissolves very readily in water.

Carbonate of lanthanum is found native in small crystalline scales, containing traces of protoxide of cerium. When obtained by precipitation, it forms a gelatinous mass, which gradually changes into shining crystalline scales (Mosander).

Sulphate of lanthanum, $LaO . SO_3$, is obtained by spontaneous evaporation in small prismatic crystals, containing 3 eq. of water of crystallization. It parts with its water at a low red heat, and with half its acid at a strong red heat. It is much less soluble in hot than in cold water (p. 559). It forms with sulphate of potash a very sparingly soluble double salt, similar to the sulphate of cerium and potassium.

Nitrate of lanthanum crystallizes in deliquescent colourless prisms, very easily soluble in water and in alcohol. When carefully heated, so as not to expel any of the acid, it fuses, and solidifies into a colourless glass on cooling. If the heat is raised, so as to drive off a portion of the acid, a fused mass remains which, on cooling, forms a kind of enamel, but almost immediately afterwards crumbles to a bulky white powder, and with such force that the particles are scattered about to a considerable distance (Mosander).

ESTIMATION OF LANTHANUM.

Lanthanum is precipitated from its solutions by potash, or by oxalate of ammonia, and the precipitate converted by ignition in a covered platinum crucible into the anhydrous oxide, containing 85·7 per cent. of the metal.

The methods of separating lanthanum from other metals are the same as those adopted for cerium. The separation of lanthanum from cerium itself may be effected by boiling the mixed oxides in a solution of chloride of ammonium (p. 559).

SECTION VII.

DIDYMIUM.

Eq. 48 *or* 600; Di.

Didymium was discovered by Mosander in 1841;* and its compounds have since been more minutely examined by Marignac.†

A pure salt of didymium is obtained by recrystallizing the rose-coloured rhombohedrons which separate from an acid solution of the mixed sulphates of lanthanum and didymium by spontaneous evaporation; and from the pure sulphate thus prepared, the other compounds of the metal may be formed.

Metallic didymium is obtained by heating potassium with an excess of chloride of didymium, and washing out the soluble chlorides with cold water. It is thus obtained, for the most part, as a grey metallic powder; but partly, also, in fused globules. The powder, thrown into the flame of a spirit-lamp, burns with bright sparks like iron-filings. The powder decomposes water at ordinary temperatures; the fused granules do not: in either form, however, the metal dissolves rapidly in dilute acids, with evolution of hydrogen.

Protoxide of didymium, DiO, 56 or 700. — Obtained in the anhydrous state by strongly igniting the nitrate, oxalate, or the precipitated hydrate in a covered crucible. It is perfectly white; is slowly converted into a hydrate by immersion in warm water; dissolves readily in the weakest acids; and expels ammonia from ammoniacal salts when boiled with them. The hydrate, DiO.HO, is a gelatinous mass resembling alumina, but having a very pale rose-colour. It contracts much by desiccation.

The *salts of didymium* have either a pure rose-colour, like the sulphate, or slightly inclining to violet, like the nitrate in the state of strong solution. *Potash, soda*, and *ammonia* precipitate the hydrate; so does *sulphide of ammonium. Carbonate of baryta* also throws down the hydrated oxide slowly, but completely. *Oxalate of ammonia* precipitates didymium completely from neutral solutions; and *oxalic acid* almost completely, unless the solution contains a large excess of acid. The *sulphates of potash, soda*, and *ammonia* form, immediately in strong, and gradually in weak solutions, rose-white precipitates of double sulphates, slightly soluble in water, less soluble in excess of the reagent; the soda-salt is the least soluble of the three. *Phosphoric* and *arsenic acids*, at a boiling heat, form precipitates sparingly soluble in acids. All compounds of didymium impart to *borax* and *phosphorus-salt* a very pale rose-colour. They do not colour carbonate of soda before the blowpipe.

Peroxide of didymium. — When the oxalate, nitrate, carbonate, or hydrate of didymium is ignited in contact with the air, and not very strongly, a dark brown

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* Pogg. Ann. lvi. 504.

† Ann. Ch. Phys. [3], xxxviii. 148; Chem. Soc. Qu. J., vi. 260.

oxide is obtained, containing from 0·32 to 0·88 per cent. of oxygen more than the protoxide. When treated with acids it dissolves readily, giving off the excess of oxygen, and forming a solution containing the protoxide. It is probably a mixture of the protoxide with a small quantity of a higher oxide of definite composition. By strong ignition in a close vessel, it is converted into the white protoxide.

Sulphide of didymium, DiS, is obtained by igniting the oxide in the vapour of bisulphide of carbon. It is a light, brownish green powder, which dissolves in acids, with evolution of hydrosulphuric acid. A greyish-white *oxysulphide*, 2DiO . DiS, is obtained by igniting the oxide with carbonate of soda and excess of sulphur, and digesting the fused mass in water (Marignac).

Chloride of didymium is obtained as a hydrate in rose-coloured crystals of considerable size, by evaporating a solution of the oxide in hydrochloric acid. The crystals, which are very soluble in water and alcohol, contain DiCl.4HO. The solution, when evaporated, gives off hydrochloric acid, and leaves an oxychloride, not however of constant composition (Marignac).

Carbonate of didymium, $DiO.CO_2$. — Precipitated as a white, bulky hydrate, tinged with rose-colour, on adding an alkaline carbonate or bicarbonate to a salt of didymium. The precipitate formed in the cold with nitrate of didymium and bicarbonate of ammonia, contains, after drying in *vacuo*, $DiO.Cl_2 + 2HO$. At 212°, it gives off 1½ eq. water and a small quantity of carbonic acid (Marignac).

Oxalate of didymium, $C_4Di_2O_8$, is precipitated from neutral solutions as a rose-white powder, which dissolves in warm nitric or hydrochloric acid, and separates, on cooling, in the form of a granular crystalline powder, sometimes even in small rose-coloured prismatic crystals. After drying in the air, it contains 8 eq. water, 6 eq. of which go off at 212° (Marignac).

Sulphate of didymium, $DiO.SO_3$. — Formed by dissolving the oxide or carbonate in dilute sulphuric acid. The solution is rose-coloured, and deposits, by spontaneous evaporation, dark rose-coloured, shining crystals, having the form of an oblique rhomboidal prism (Mosander), and cleaving readily and distinctly in a direction parallel to the base. They contain $3(DiO.SO_3) + 8Aq.$, and give off the whole of their water at 392° F. (200° C.), leaving an anhydrous powder, which may be heated to redness without further alteration. A solution of the sulphate, when heated, especially to the boiling point, deposits a crystalline precipitate containing $DiO.SO_3 + 2HO$. The following table exhibits the solubility of the anhydrous salt, and of the two crystalline hydrates in water at different temperatures:—

Temperature.	Anhydrous Sulphate.	Sulphate with 2 eq. water.	Sulphate crystallized in the cold.
12° C	43·1	—	—
14	39·3	—	—
18	25·8	16·4	—
19	—	—	11·7
25	20·6	—	—
38	13·0	—	—
40	—	—	8·8
50	11·0	—	6·5
100	—	—	1·7

The anhydrous sulphate, exposed to the heat of an intense charcoal fire, gives off two-thirds of its sulphuric acid, and leaves a *tribasic sulphate*, $3DiO.SO_3$ (Marignac).

Sulphate of didymium, mixed in solution with *sulphate of potash*, forms a crystalline double salt, which appears to contain $KO.SO_3 + 3(DiO.SO_3) + 2HO$; it dissolves in sixty-three times its weight of cold water. With *sulphate of soda* it forms the anhydrous double salt, $NaO.SO_3 + 3(DiO.SO_3)$, which requires two hundred times its weight of water to dissolve it, and is still less soluble in a solution of sulphate of soda. With *sulphate of ammonia,* it forms the salt $NH_4O.SO_3 + 3(DiO.SO_3) + 8HO$ soluble in eighteen times its weight of water (Marignac).

Sulphite of didymium, $DiO.SO_2 + 2HO$. — Oxide of didymium suspended in water, is readily dissolved by a stream of sulphurous acid gas, forming a rose-coloured solution which becomes turbid when heated, forming a light bulky precipitate, which redissolves as the liquid cools, unless the temperature has been raised to the boiling point, in which case it remains undissolved (Marignac).

Nitrate of didymium, $DiO.NO_5$. — This salt is very soluble in water and in alcohol of the strength of 96 per cent. The aqueous solution has a pure rose colour when dilute, but appears violet by reflected light when strong. A syrupy solution solidifies on cooling into a deliquescent crystalline mass, which, when carefully heated to 300° C., melts, becomes perfectly anhydrous, and exhibits the composition of the neutral nitrate. At a higher temperature, it is decomposed, giving off nitrous fumes, and leaving a residue from which water extracts a portion of neutral nitrate, and leaves a basic salt containing $4DiO.NO_5 + 5HO$. (Marignac).

Phosphate of didymium, $3DiO.PO_5 + 2HO$. — Precipitated, after a few hours, as a white powder, on adding a strong solution of phosphoric acid to a strong solution of nitrate of didymium. It is insoluble in water, very sparingly soluble in dilute acids; but dissolves readily in the stronger acids when concentrated; gives off its water when ignited (Marignac).

Arseniate of didymium, $5DiO.2AsO_5 + 2HO$.—Obtained as a pulverulent precipitate by the action of arsenic acid on solutions of didymium at the boiling heat, or as a gelatinous precipitate by the action of neutral arseniate of potash at ordinary temperatures. It is but slightly soluble in dilute acids (Marignac).

The *quantitative estimation* of didymium is effected in the same manner as that of lanthanum. The anhydrous protoxide contains 85·7 per cent. of the metal.

The methods of separating didymium from the preceding metals are also the same as for lanthanum. For separating it from lanthanum itself, no method has yet been devised sufficiently exact for quantitative analysis.

SECTION VIII.

TANTALUM.

Eq. 68·82 *or* 860·3; Ta.

This metal was discovered by Ekeberg in 1802. It is a rare metal, occuring only in a few minerals, the principal of which are Swedish *tantalite* and *yttro-tantalite.*

Tantalum is obtained, in the metallic state, by heating the fluoride of tantalum and potassium, or fluoride of tantalum and sodium, with sodium, in a well covered iron crucible, and afterwards washing out the soluble salts by water. The reduced metal thus obtained is not quite pure, being more or less contaminated with acid tantalate of soda, the quantity of which may, however, be diminished by covering the mixture in the crucible with chloride of potassium.

Tantalum is a black powder, which, according to H. Rose, is a good conductor of electricity. When heated in the air, it burns with a bright light, and is converted, though with difficulty, into tantalic acid. It is not attacked by sulphuric, hydrochloric, or nitric acid, or even by aqua regia. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum forms two compounds with oxygen, viz., *tantalous acid,* probably TaO, and *tantalic acid,* TaO_2.

Tantalous acid is obtained by placing tantalic acid in a small cavity in a crucible filled with charcoal, and exposing it to the strongest heat of a blast-furnace; a thin film on the outside is at the same time reduced to the state of metal. It is a dark grey mass which scratches glass, and acquires metallic lustre by burnishing.

Tantalic acid, TaO_2; 84·82 or 1060·3.*—This compound is formed when tantalum burns in the air; also by the action of water on chloride of tantalum; and, in the form of a potash-salt, by fusing metallic tantalum or tantalous acid with hydrate, carbonate, or bisulphate of potash. It exists, in combination with various bases, in the minerals above mentioned, and is usually extracted from tantalite, which contains the oxides of iron and manganese, together with small quantities of stannic and tungstic acids, by one of the following processes:—1. The mineral, after being pulverized and levigated, is fused with twice its weight of hydrate of potash; the fused mass digested in hot water; and the filtered solution supersaturated with hydrochloric or nitric acid: hydrated tantalic acid is then precipitated in white flakes, which may be purified by washing with water (Berzelius). 2. A better method, however, is to fuse the levigated tantalite in a platinum crucible with six or eight times its weight of bisulphate of potash; pulverize the mass when cold; and boil it repeatedly with fresh quantities of water till no more sulphate of potash, iron, or manganese is dissolved out of it. The residue, which consists of hydrated tantalic acid mixed with ferric oxide, stannic acid, and tungstic acid, is then digested in sulphide of ammonium containing excess of sulphur, which removes the stannic and tungstic acids, and converts the iron into sulphide; the liquid is filtered, and the tantalic acid washed with water containing sulphide of ammonia, then boiled with strong hydrochloric acid to remove the iron, and finally washed with boiling water. The hydrated tantalic acid thus prepared is converted into the anhydrous acid by ignition. It may still, however, contain silica, to remove which, it is dissolved in aqueous hydrofluoric acid, the filtered solution mixed with sulphuric acid and evaporated to dryness, and the residue ignited as long as its weight continues to diminish: the silica is then expelled as gaseous fluoride of silicon (Berzelius).

Anhydrous tantalic acid is a white powder, which remains white when heated, or acquires but a very faint tinge of yellow. Its specific gravity varies from 7·022 to 8·264, increasing with the temperature to which the acid has been exposed (H. Rose). It neither melts nor volatilizes when heated, and is destitute of taste and smell. It is reduced to the metallic state in the circuit of a very powerful voltaic battery; partially also by very strong ignition in contact with charcoal. When ignited in the vapour of bisulphide of carbon, it yields sulphide of tantalum:

$$2TaO_2 + 4CS_2 = Ta_2S_3 + 4CO + 5S.$$

It is insoluble in all acids, and can only be rendered soluble by fusion with hydrate or carbonate of potash.

Hydrated tantalic acid, obtained by precipitating an aqueous solution of tantalate of potash with hydrochloric acid, or by decomposing chloride of tantalum with water containing a small quantity of ammonia, is a snow-white bulky powder, which reddens litmus-paper while moist, and dissolves in hydrochloric and hydro-

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* The composition of tantalic acid is usually represented by the formula TaO_3, which, according to the original analysis of that compound by Berzelius (88·5 per cent. tantalum + 11·5 per cent. oxygen), gives for tantalum the equivalent number 185. But according to the recent experiments of H. Rose (Berl. Akad. Ber., 1856, 385), the tantalum-compounds appear to contain 2 eq. of the chlorous element, viz., the chloride, $TaCl_2$, tantalic acid, TaO_2, &c.; he also finds the chloride to contain 49·25 per cent. of tantalum, making the equivalent of tantalum 68·82.

fluoric acids. When strongly heated it gives off its water and becomes incandescent. The hydrate, obtained by fusing tantalite with bisulphate of potash in the manner above described, is of a denser and more crystalline character, is insoluble in all acids excepting strong sulphuric acid, and is precipitated from the solution by water. When heated, it becomes anhydrous, but does not emit light.

Tantalic acid combines with *bases* much more readily than with acids. When fused with *hydrate of potash* in a silver crucible, it forms a transparent mass of tantalate of potash, which, after cooling, dissolves completely in water. With *hydrate of soda* it fuses into an opaque turbid mass, and ultimately deposits a sediment, which is not taken up by fusion with any excess of the alkali. Water poured upon the fused mass when cold dissolves out the excess of soda, but not a trace of tantalic acid; and the residue, when treated with fresh water, dissolves and forms an opalescent solution of acid tantalate of soda, which salt is completely insoluble in a strong solution of caustic soda, and is therefore precipitated on mixing the liquid with the solution of soda previously obtained by treating the fused mass with water. When tantalic acid is fused with *carbonate of potash* or *soda*, the fused mass is not completely soluble in water.

Hydrochloric acid, added in excess to the solution of an alkaline tantalate, first precipitates the tantalic acid, and then redissolves it, forming a slightly opalescent liquid. *Sulphuric acid* also precipitates the tantalic acid, but does not redissolve it when added in excess. *Carbonic acid gas*, passed through the solution of an alkaline tantalate, precipitates the whole of the tantalic acid in the form of an acid salt. *Chloride* or *sulphate of ammonium* also precipitates the tantalic acid from these solutions in the form of hydrate, mixed with small quantities of ammonia and the fixed alkali. The presence of carbonate of potash or soda prevents the formation of this precipitate at ordinary temperatures; but it then appears after boiling for some time. Sulphide of ammonium produces no precipitate. *Chloride of barium* or *calcium* forms a precipitate of tantalate of baryta or lime, insoluble in water and in ammoniacal salts. *Nitrate of silver* forms, in the solution of a neutral alkaline tantalate, a white precipitate, which is turned brown by a small quantity of ammonia, and dissolves in a larger quantity. A solution of *basic mercurous nitrate* forms a yellowish white precipitate, which turns black when heated. *Ferrocyanide of potassium*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; *ferricyanide of potassium* a white precipitate. *Infusion of galls*, added to a solution of an alkaline tantalate acidulated with sulphuric or hydrochloric acid, forms a light yellow precipitate soluble in alkalies. *Zinc*, immersed in the solution of an alkaline tantalate acidulated with hydrochloric acid, does not produce any blue colour; neither is that colour produced, or but very faintly, on addition of sulphuric acid. But if chloride of tantalum be dissolved in strong sulphuric acid, and then water and metallic zinc added, a fine blue colour is produced, which does not change to brown, but soon disappears. The blue colour is also produced on placing zinc in a solution of chloride of tantalum in hydrochloric acid, to which a small quantity of water has been added; too much water, however, prevents its formation.

Before the blowpipe tantalic acid dissolves abundantly in *phosphorus-salt*, forming a clear, colourless glass, which undergoes no alteration when heated in the inner flame, and does not turn red on addition of protosulphate of iron. With *borax* also it forms a transparent glass, which, however, if the quantity of tantalic acid is somewhat large, may be rendered opaque by interrupted blowing, or *flaming*, as it is technically called, but recovers its transparency by long exposure to a continued blast. A very large quantity of tantalic acid renders the glass opaque. No alteration takes place in the inner flame. With *carbonate of soda* on charcoal, tantalic acid produces effervescence, but does not fuse into a bead or undergo reduction.

The above-described characters are sufficient to distinguish tantalic acid from all the substances previously described. From titanic acid, which it most resembles, it is distinguished, first, by its behaviour before the blowpipe; secondly, by its perfect insolubility in strong sulphuric acid after ignition, ignited titanic acid, when finely pulverized, being soluble in that acid; and, thirdly, by the fact that, when it is fused with bisulphate of potash, and the fused mass treated with cold water, the tantalic acid remains undissolved in combination with sulphuric acid; whereas titanic acid, similarly treated, yields a fused mass, which dissolves completely in a considerable quantity of cold water, provided the fusion has been continued long enough. From silica, tantalic acid is distinguished by its behaviour before the blowpipe; silica being insoluble in phosphorus-salt, and fusing to a transparent bead when heated on charcoal with a small quantity of carbonate of soda. The behaviour of tantalic acid with zinc, with tincture of galls, and with hydrofluoric acid, also distinguishes it from silica.

Sulphide of tantalum, Ta_2S_3.—Obtained by igniting tantalic acid in the vapour of bisulphide of carbon, or by exposing chloride of tantalum to the action of hydrosulphuric acid gas. The product is not perfectly definite in either case. The second process yields a sulphide containing 24·08 per cent. sulphur, whereas the formula Ta_2S_3, requires 25.86 per cent. The former process gives a product containing 28·5 per cent. sulphur. Sulphide of tantalum is a black substance, which acquires a brass-yellow colour by trituration in an agate mortar. Heated in an atmosphere of chlorine gas, it is converted into chloride of tantalum and chloride of sulphur (H. Rose).

Chloride of tantalum, $TaCl_2$. — Prepared by passing chlorine gas over a heated mixture of tantalic acid and charcoal. Tantalic acid is mixed with starch or sugar, and the mixture completely charred by ignition in a covered crucible. It is then introduced in small pieces into a glass tube which is strongly heated by a charcoal fire, while a stream of dry carbonic acid is passed through it. As soon as all the moisture is expelled, the tube is left to cool, the flow of carbonic acid being still kept up; the carbonic acid apparatus is then replaced by a chlorine apparatus, and the tube again heated after the carbonic acid and atmospheric air have been completely expelled by the chlorine. Chloride of tantalum is then obtained in the form of a sublimate of a pure yellow colour. If, however, the tantalic acid contains tungstic acid, the colour of the sublimate is red; and if stannic or titanic acid is present, yellow drops of liquid chloride are also produced. Chloride of tantalum melts at 430°, and volatilizes at 291°. Water decomposes it, forming hydrochloric and tantalic acids; but the decomposition is not complete even at the boiling heat: water containing a small quantity of ammonia decomposes the chloride perfectly even at ordinary temperatures. According to the recent experiments of H. Rose, chloride of tantalum contains 81·14 per cent. of tantalum.

Bromide of tantalum is prepared in the same manner as the chloride; when freed from excess of bromine, it has a yellowish colour.

Fluoride of tantalum, TaF_2.—Ignited tantalic acid does not dissolve in aqueous hydrochloric acid; but the hydrate dissolves, forming a clear solution, which, when evaporated, partly gives off the tantalum as fluoride, but also leaves a white residue of oxyfluoride. Fluoride of tantalum forms with fluoride of potassium a crystalline double salt, containing $KF.2TaF_2$; and with fluoride of sodium the salt, $NaF.TaF_2$ (H. Rose).

ESTIMATION AND SEPARATION OF TANTALUM.

Tantalum is estimated in the form of anhydrous tantalic acid, containing 81·13 per cent. of the metal. It occurs in nature associated with lime, magnesia, yttria, and the oxides of iron and manganese, and occasionally with zirconia, titanic acid, and a few other substances. From these it is separated by fusion with hydrate of potash, or, better, with bisulphate of potash, in the manner already described (567). Some compounds of tantalic acid may be decomposed by sulphuric acid, the tantalic acid being separated in the insoluble state, and all the bases passing into the solution.

Tantalate of *zirconia* may be decomposed in this manner. On treating that compound with strong sulphuric acid, and digesting the cooled mass for some time with a large quantity of water, sulphate of zirconia dissolves, and tantalic acid remains behind in combination with sulphuric acid, from which it may be purified by repeated boiling with water.

From *titanic acid*, with which it sometimes occurs in nature, tantalic acid is separated by fusing the mineral with bisulphate of potash, and treating the fused mass with a large quantity of water. Titanic acid then dissolves, especially if the water is slightly acidulated with hydrochloric acid, while sulphate of tantalic acid remains undissolved. The titanic acid is precipitated from the solution by boiling: the separation is, however, not very complete. In some cases, the decomposition may be effected by sulphuric acid.

From the *alkalies*, tantalic acid may be completely separated by sulphuric acid, provided the compound is soluble in water. In the contrary case, it must first be fused with carbonate or hydrate of potash. If, however, the quantity of alkali is to be likewise estimated, the compound must be rendered soluble by fusion with sulphate of ammonia.*

SECTION IX.

COLUMBIUM.

Synonyme. Niobium; Cb.

This metal was discovered by Hatchett in 1801, in a black mineral (columbite), from Massachusetts, in North America; it was thence named *Columbium.* Wollaston, in 1809, examined it further, and pronounced it to be identical with the tantalum discovered by Ekeberg, in Swedish tantalite. This idea of the identity of the two metals remained current till 1846, when H. Rose,† by a more careful investigation of the matter, was led to conclude that the American columbite, and the tantalite from Bodenmais, in Bavaria, contained two acids bearing a very close resemblance to tantalic acid, but nevertheless, distinct from it and from each other. To the metals supposed to exist in these acids he assigned the names *Niobium* and *Pelopium.* But by a later investigation,‡ he finds that these two acids really contain the same metal, associated with different quantities of oxygen; he therefore discards the name pelopium, and proposes to designate by *niobium* the metal contained in American columbite and Bavarian tantalite. As, however, this metal is clearly the one discovered fifty years ago by Hatchett, we cannot do better than retain for it the name originally proposed by its discoverer, viz., COLUMBIUM.§

Columbium likewise occurs, associated with yttrium, uranium, iron, and small quantities of other metals, in a Siberian mineral called urano-tantalite, yttro-ilmenite, or samarskite; also in pyrochlore, eukolite or wöhlerite, euxenite, and in a variety of pitchblende from Satersdälen.

Metallic columbium is obtained by passing dry ammoniacal gas over the chloride. It is a black powder, which oxidizes when heated in the air. Nitric acid and aqua-regia have no effect upon it; but a mixture of hydrofluoric and nitric acids attacks it at ordinary temperatures. It combines with oxygen in two proportions, forming *columbous* and *columbic* acids, formerly supposed by Rose to

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* H. Rose, Handb. d. Anal. Chem. 1851, ii. 326–335.

† Pogg. Ann. lxiii. 317; lxix. 115.

‡ Pogg. Ann. xc. 456; Ann. Ch. Pharm. lxxxviii. 245.

§ See a paper "On the Nomenclature of the Metals contained in Columbite and Tantalite," by Prof. Connell, Phil. Mag. [4].

contain different metals, and called respectively niobic and pelopic acids. The composition of these acids has not yet been determined.

Columbous acid, or a mixture of that acid with columbic acid, is separated from the minerals containing it by processes similar to those already described for the preparation of tantalic acid (p. 567); and when the acid, or mixture of acids, thus obtained, is mixed with charcoal and heated in a stream of chlorine gas, with the precautions already detailed for the preparation of chloride of tantalum (p 570), it is generally converted into two chlorides, — the one white, volatile, but not fusible; the other yellow, likewise volatile, and easily fusible; the latter contains the larger proportion of chlorine. It was the formation of these two chlorides which led Rose to conclude that certain varieties of tantalite contained two distinct metals, niobium and pelopium; he now finds, however, that the substance which he regarded as perfectly pure niobic acid, obtained by the action of water on the white chloride, may, by mixing it with a large excess of charcoal, and gently igniting the mixture in a stream of chlorine gas, with strict attention to all the precautions above alluded to, be completely converted into the yellow chloride, — the so-called chloride of pelopium. But if a smaller quantity of charcoal be used, or if the mixture be too strongly ignited during the action of the chlorine, especially at the commencement, the white and less volatile chloride (chloride of niobium), is obtained, as well as the yellow compound.

Columbium appears, then, to be capable of uniting with chlorine in two proportions; and the chlorides thus formed yield, when treated with water, two acids of corresponding constitution, viz., *Columbous* and *Columbic acids*, the latter, which contains the larger proportion of oxygen, being formed from the yellow chloride.

Columbous acid (Rose's niobic acid) may, like tantalic acid, be obtained in the amorphous and the crystalline state, viz., by the rapid or gradual action of water on the chloride. Its specific gravity is lower than that of tantalic acid, and is subject to similar variations. Samples of the acid, prepared from various sources, exhibited, after ignition over a spirit-lamp to the point of incandescence, specific gravities ranging from 4·66 to 5·26; by stronger ignition, the density was diminished. The mean density of the amorphous acid was found to be greater than that of the crystalline in the ratio of 1 to 0·875. The acid is colourless both in the anhydrous and hydrated states, but when heated assumes a yellow colour, much deeper than that of heated tantalic acid. The hydrated acid becomes incandescent during its transition to the anhydrous state.

Columbous acid is decomposed by ignition in a stream of hydrosulphuric acid, and converted into sulphide of columbium. When ignited in ammoniacal gas, it turns black, and yields a large quantity of water.

Columbous acid, after ignition, is insoluble in all acids. The hydrated acid is but very sparingly soluble in hydrochloric acid; so that when an alkaline columbite is precipitated by excess of hydrochloric acid, the filtrate retains only a trace of columbous acid in solution. The hydrated acid dissolves, to a certain extent, in oxalic and in hydrofluoric acid.

The *alkaline columbites* are soluble in water, in solutions of potash and carbonate of potash, but dissolve with great difficulty in excess of soda and carbonate of soda, more sparingly even than tantalate of soda. Columbous acid is precipitated from its alkaline solutions by acids, especially by sulphuric acid, even at ordinary temperatures; whereas the precipitation of tantalic acid requires the aid of heat. Oxalic acid does not affect alkaline columbites; but *carbonic acid* gas precipitates an acid salt soluble in a large quantity of water; *acetic acid* and *salammoniac* also form precipitates. A solution of an alkaline columbite, acidulated with sulphuric or hydrochloric acid, forms a red precipitate with *ferrocyanide of potassium*, bright yellow with the *ferricyanide*, and orange-red with *infusion of galls*. A piece of *zinc*, immersed in the acidulated solution, forms a beautiful blue precipitate, which after a while changes to brown.

Before the blowpipe, especially in the inner flame, columbous acid assumes a greenish yellow colour while hot, but becomes colourless on cooling. With *borax* it forms in the outer flame a colourless bead, which, if the acid is in sufficient quantity, becomes opaque by flaming. In the inner flame, the bead assumes a greyish blue colour, provided it contains a sufficient quantity of acid to produce opacity on cooling. In *phosphorus-salt*, the acid dissolves in large quantity, forming a colourless bead in the outer flame, and in the inner, a violet-coloured, or, if the bead be saturated with the acid, a beautiful blue bead, the colour disappearing in the outer flame. The addition of protosulphate of iron changes the colour to blood-red. These characters, together with the above-mentioned precipitates, sufficiently distinguish columbous from tantalic acid.

Columbic acid (Rose's pelopic acid) bears a very strong resemblance to tantalic acid, and is intermediate in its properties between that acid and columbic acid. Its specific gravity ranges from 5·5 to 6·7. It appears to be susceptible of three modifications; viz., amorphous, crystalline before ignition, and crystalline after ignition at the heat of a porcelain-furnace. It is insoluble in all acids after ignition. It is precipitated from its alkaline solutions by the same reagents as columbous acid. The precipitate formed by hydrochloric acid redissolves in excess, forming an opalescent solution from which the acid is completely precipitated by sulphuric acid at a boiling heat. The acidulated solutions yield a brownish-red precipitate with *ferrocyanide of potassium*, white with *ferricyanide*, and orange-yellow with *infusion of galls*. *Zinc* behaves with these solutions in the same manner as with solutions of tantalic acid. A fine blue colour is obtained by treating the yellow chloride of columbium with hydrochloric acid, diluting with water, and adding a piece of zinc.

With *borax* before the blowpipe, columbic acid behaves like tantalic acid. In *phosphorus-salt* it dissolves in large quantity, forming a colourless bead in the outer flame. In the inner flame, the bead assumes a light-brown colour, tinged with violet, the colour disappearing again after a while in the outer flame. The addition of protosulphate of iron changes the brown colour to crimson.

It is remarkable that columbic acid cannot be formed directly from columbous acid, even by the most powerful oxidizing agents. It appears, however, to be deprived of a portion of its oxygen by certain reducing agents.

The methods of estimating columbium and separating it from other metals are the same as for tantalum. No method is known of separating columbium from tantalum; but these metals have not hitherto been found occurring together.

Ilmenium.(?)—According to the observations of R. Hermann,* it would appear that Siberian yttrotantalite or yttroilmenite contains a peculiar metal, ilmenium, which forms an acid, ilmenic acid, very closely resembling columbous acid, but nevertheless distinct from it; the chief points of difference being the lower specific gravity, viz., 4·1 to 4·2; the insolubility of the hydrate in hydrochloric acid; and the formation of a compound with sulphuric acid which is decomposed by a large quantity of water, leaving a residue of hydrated ilmenic acid. H. Rose,† however, is of opinion that the supposed ilmenic acid is merely columbous [niobic] acid, more or less impure. The question must, for the present, be regarded as undecided. Rose likewise regards yttroilmenite as identical with urano-tantalite or samarskite.

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* J. pr. Chem. xxxviii. 91, 119; xl. 475; lxv. 54.

† Pogg. Ann. lxxi. 157.

ORDER VIII.

METALS WHOSE OXIDES ARE REDUCED TO THE METALLIC STATE BY HEAT, (NOBLE METALS).

SECTION I.

MERCURY.

Eq. 100 *or* 1250; Hg.

Mercury, or quicksilver, as it is named from its fluidity, has been known from all antiquity. It is found to a small extent in the metallic state, but its principal ore is the native sulphide, *cinnabar.* The most valuable European mines of mercury are, those of Almaden in Spain, and of Idria in Illyria. At Almaden the cinnabar is found in veins, often nearly fifty feet thick, traversing micaceous schists of the older transition period: in Illyria it is disseminated in beds of grit, bituminous schist, or compact limestone of more recent date. The mode of extraction in both these localities, consists in simply roasting the ore in a distillatory apparatus, whereby the sulphur is burned and converted into sulphurous acid, while the mercury is set free in the form of vapour, and condenses in chambers or vessels provided for it.

The arrangement adopted in Illyria is represented in figures 197, 198, 199. A is a large furnace (figs. 197 and 199), on each side of which is a series of condensing

Fig. 197.

Fig. 198.

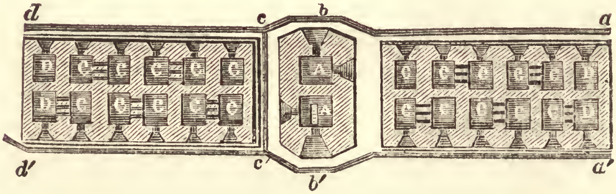
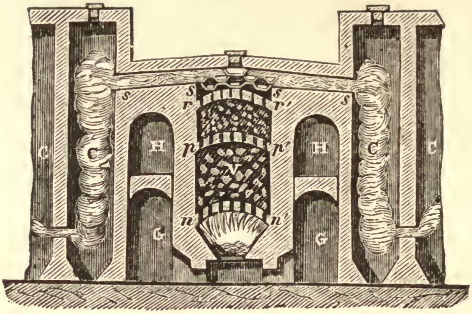


Fig. 199.



chambers, C C C C C D. The space V, separated from the fire-place by the perforated arch $n\,n'$, is filled with the ore in large lumps; smaller pieces are introduced into the next compartment above the arch $p\,p'$; and on the uppermost arch, $r\,r'$, are laid a number of earthen capsules, containing the pulverized ore and the mercurial residues of preceding operations. The fire being lighted, and the heat gradually raised, the sulphur is burned by the air which enters through channels opening into the spaces G, H; and the mixture of mercurial vapour, sulphurous acid, and smoke from the fire, passes through the horizontal channel at the top of the furnace, then up and down through the condensing chambers, C C C C, and finally escapes into the air.

The greater part of the mercury condenses in the first three chambers, whence it runs into the channels $a\ b\ c\ d$, $a'\ b'\ c'\ d'$, which conduct it into a reservoir. To facilitate the condensation of the last portions of mercury in the chambers D D, the vapours are made to pass between a series of boards placed from side to side of these chambers in an inclined position, and having a stream of water continually running over them. As the mercury which condenses in these last chambers is mixed with a considerable quantity of dust, it is collected in separate channels, then filtered, and the residues returned to the furnace as already described.

The mercury obtained by this process is purified by filtratation through coarse linen cloth, and sent into the market in wrought-iron bottles, each containing about fifty pounds.

At Almaden, the mercury is also extracted from the cinnabar by roasting, the operation being conducted in furnaces called *buytrones.* (Figs. 200 and 201.)

Fig. 200.

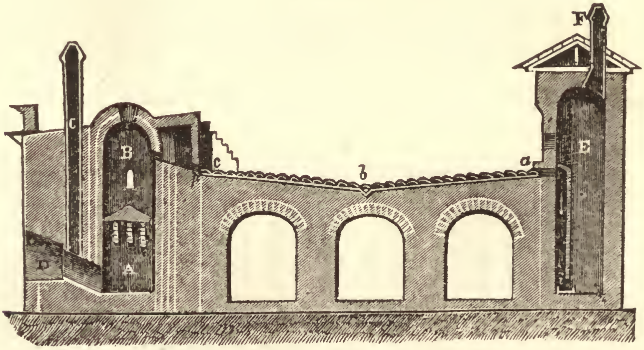
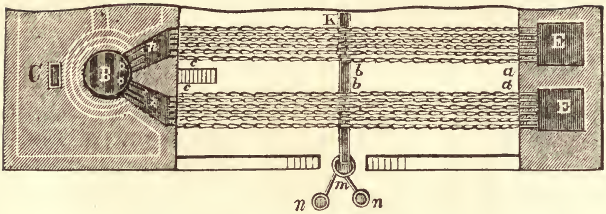


Fig. 201.

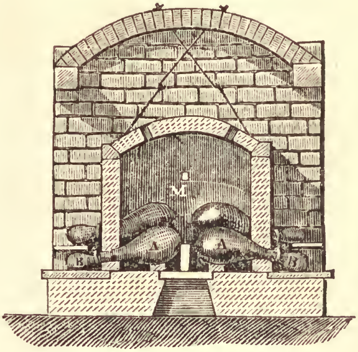


The fire is made at A, and the space B, above it, is filled with the ore, the largest pieces being laid on the perforated arch at the bottom, smaller pieces above, and the whole covered with lumps of a mixture of clay, powdered ore, and the residues of preceding operations. The vapours pass through an aperture *p*, in the upper part of the furnace, into a series of tubular vessels called *aludels*, open at both ends and fitting one into the other. These are laid on a surface *c*, *b*, *a*, called the *aludel-bath*, first descending a little, then ascending, and finally opening into the chimney. The form and disposition of the aludels is shown in figure 202. The condensed mercury escapes at the joints of the aludels, and runs into the channel *b b*, by which it is conveyed into the reservoirs *m*, *n n*. The uncondensed mercurial vapour passes into the chamber E, where it deposits a mercurial dust, which yields by filtration an additional quantity of liquid mercury, and a residue which is mixed with clay and pounded ore, and returned to the furnace in the manner above mentioned. The heating of the furnace is continued for twelve or thirteen hours: it is then left to cool for three or four days, after which it is cleared out and arranged for another operation.

Fig. 202.

In the duchy of Deux Ponts, a mixture of cinnabar and limestone is heated to redness in retorts of earthenware or cast-iron, placed side by side in an oblong furnace (fig. 203), and provided with receivers containing a certain quantity of water. Sulphide of calcium and sulphate of lime are then formed, and the mercury is evolved in vapour, which condenses in the receivers.

Fig. 203.



At Horzowitz, in Bohemia, a mixture of cinnabar and smithy-scales is placed in iron dishes, which are attached one above the other by the centres of their bases to a vertical iron axis, and covered with an iron receiver, closed at top and dipping into water at the bottom. The upper part of the receiver is surrounded by the furnace, and imparts its heat to the dishes, from which the mercury rises in vapour and collects in the water below.

The mercury of commerce is generally very pure; it is sometimes, however, contaminated with foreign metals, and in that case its fluidity is remarkably impaired.

Mercury may be purified by distilling it from half its weight of iron-turnings, or by digesting it with a small quantity of nitric acid, or with a solution of corrosive sublimate, which rids it of metals more oxidable than itself. The purification may also be effected by agitating the mercury with a small quantity of solution of sesquichloride of iron. Pure mercury should leave no residue when dissolved in nitric acid, evaporated, and ignited; when made to run down a slightly inclined surface, it should retain its round form, and not *drag a tail;* and when agitated in a bottle with dry air, it should not yield any black powder.

Mercury is liquid at ordinary temperatures. Its colour is white, with a shade of blue when compared with that of silver, and it has a high metallic lustre. At 39° or 40° below zero, it becomes solid, and crystallizes in regular octohedrons. According to M. Kupffer, the density of mercury at 39·2° is 13.5886; at 62.6°, 13·5569; and at 78·8°, 13·535 (according to Kopp, it is 13·595 at 39·2°). In the solid state, its density is about 14·0. Mercury boils at 662°, forming a colourless vapour, the density of which was observed, by Dumas, to be 6976; the theoretical density is 6930. Mercury emits a sensible vapour between 68° and 80°, but not under 20° (Faraday). When heated near its boiling point, mercury absorbs oxygen from the air, and forms crystalline scales of the red oxide. It is not affected by boiling hydrochloric or dilute sulphuric acid, but is readily dissolved by dilute nitric acid. This metal never dissolves in hydrated acids by substitution for hydrogen. Mercury combines with oxygen in two proportions, forming the black oxide, Hg_2O, and the red oxide, composed of single equivalents, HgO, both of which are bases. According to these formulæ, the equivalent of mercury is assumed to be 100; but whether it should be this number or a multiple of it by 2, no certain means exist of deciding, while we are in ignorance of any isomorphous relation of mercury with the magnesian metals.

MERCUROUS COMPOUNDS.

Dioxide of mercury (*black oxide*), *Mercurous oxide*, Hg_2O, 208 or 2600.— This oxide is obtained by the action of a cold solution of potash, used in excess, upon calomel. The substances should be mixed briskly together in a mortar, in order that the decomposition may be as rapid as possible, and the oxide be left to dry spontaneously in a dark place. Mr. Donovan finds these precautions necessary, from the disposition of this oxide to resolve itself into metallic mercury and the higher oxide. The decomposition of mercurous oxide is promoted by elevation of temperature, and by exposure to light.

Mercurous oxide is a black powder, whose density is 10·69 (J. Herapath); it unites with acids and forms salts. Its soluble salts are all partially decomposed by pure water, which combines with a portion of their acid, and throws down a subsalt containing an excess of oxide. They are precipitated black by *hydrosulphuric acid* and *alkaline sulphides. Caustic alkalies* throw down a black precipitate of mercurous oxide. The *alkaline carbonates* precipitate white mercurous carbonate, which soon turns black from decomposition. *Carbonate of baryta* also decomposes mercurous salts, forming a mercuric salt, which remains in solution, and a precipitate of metallic mercury. Mercurous salts are decomposed by *hydrochloric acid* and soluble *chlorides,* with precipitation of calomel as a white powder, a property by which they are distinguished from the salts of the red oxide of mercury. In very dilute solutions, only an opalescence is produced. The precipitate turns black when treated with potash or ammonia. Mercurous salts form with *phosphate of soda* a white precipitate of mercurous phosphate, and with *alkaline chromates,* a brick-red precipitate of mercurous chromate. *Oxalic acid* and *alkaline oxalates* form a white precipitate of mercurous oxalate. *Ferrocyanide of potassium* produces a thick white precipitate, and *ferricyanide of potassium* a red-brown precipitate. *Tincture of galls* yields a brownish-yellow precipitate.

The salts of this, and also of the red oxide, are reduced to the metallic state by copper and the more oxidable metals, and by the proto-compounds of tin; also by phosphorous and sulphurous acids. The precipitated mercury often takes the form of a grey powder, in which no metallic globules are perceptible, and remains in this condition while moist. Mercury in this divided state possesses the medicinal qualities of the milder mercurials, and has often been mistaken for black oxide.

To obtain *precipitated mercury*, equal weights of crystallized protochloride of tin (salt of tin) and corrosive sublimate may be dissolved, the first in dilute hydrochloric acid and the second in hot water, and the solutions mixed, with stirring. The salt of tin takes up all the chlorine of the corrosive sublimate, becoming bichloride of tin, which remains in solution, while the mercury is liberated, and forms so fine a precipitate, that it requires several hours to subside. It may be washed by affusion of hot water and subsidence, and slightly drained on a filter, but not allowed to dry. There can be no doubt that it is in this divided state, and not as the black oxide, that mercury is obtained by trituration with fat, turpentine, syrup, saliva, &c., in many pharmaceutical preparations.

Disulphide of mercury, Hg_2S, is obtained, as a black precipitate, by the action of hydrosulphuric acid on a solution of mercurous nitrate or upon calomel. This sulphide is decomposed by a gentle heat, and resolved into globules of mercury and the higher sulphide.

Dichloride of mercury, Mercurous chloride, Calomel, Hg_2Cl, 235·5 or 2943·75. — A variety of processes are given for the preparation of this remarkable substance. It may be obtained in the humid way, by digesting $1\frac{1}{8}$ parts of mercury with 1 part of pure nitric acid, of density from 1·2 to 1·25, till the metal ceases to dissolve, and the liquid has begun to assume a yellow tint. A solution is also prepared of 1 part of chloride of sodium in 32 parts of distilled water, to which a certain quantity of hydrochloric acid is added; and this, when heated to near the boiling point, is mixed with the mercurial salt. The mercury takes up the chlorine of the common salt, and the subchloride of mercury formed precipitates as a white powder, while the nitric acid and oxygen are given up by the mercury to the sodium, which becomes nitrate of soda:

$$NaCl + Hg_2O.NO_5 = Hg_2Cl + NaO.NO_5.$$

The excess of acid in this process is intended to prevent the precipitation of any subnitrate of mercury, which the dilution of the nitrate of mercury, on mixing the solutions, might occasion. Calomel is also obtained by rubbing together, in a mortar, 4 parts of protochloride of mercury (corrosive sublimate) with 3 parts of running mercury. The mixture is afterwards introduced into a glass balloon, and sublimed by a heat gradually increased. Here the protochloride of mercury combines with mercury, and the dichloride is produced. The same result is obtained by mixing mercuric sulphate with as much mercury as it already contains, and about one-third of its weight of chloride of sodium, and subliming the mixture. The vapour of the dichloride of mercury, in these sublimations, is advantageously condensed by conducting it into a vessel containing hot water; the vapour of the water then condenses the salt in an extremely fine and beautifully white powder. The product of this operation is recommended by its purity, as well as by its minute division; for the water dissolves out all the protochloride of mercury by which the dichloride is accompanied. It appears that whenever the dichloride is sublimed, a small portion of it is resolved into mercury and the protochloride. As the calomel usually condenses in a solid cake, it must, to prepare it for medical use, be reduced to a fine powder, and washed with hot water to remove the soluble chloride.

Dichloride of mercury is obtained by sublimation, in four-sided prisms, terminated by summits of four faces. When the solid cake is finely pounded, the salt acquires a yellow tinge. The density of this salt in the solid condition is 6·5; in the state of vapour 8350. One volume of the vapour contains one volume of vapour of mercury and half a volume of chlorine. This salt is so very sparingly soluble in water, that when mercurous nitrate is added to hydrochloric acid diluted even with 250,000 times its weight of water, a sensible precipitate of dichloride of mercury appears. When boiled for a long time in hydrochloric acid, this salt is resolved into protochloride of mercury which dissolves, and mercury which is reduced.

Action of ammonia on dichloride of mercury. — The dry dichloride was found by Rose to absorb an equivalent of ammonia, and to become black. Exposed to air, the compound loses its ammonia, and the dichloride of mercury recovers its white colour. This ammoniacal compound is $Hg_2Cl.NH_3$, and may be regarded as $\left.\begin{matrix}\overbrace{NH_3Hg}\\ \quad Hg\end{matrix}\right\}$ Cl, that is, as dichloride of mercury in which 1 eq. of mercury is replaced by mercurammonium, $\overbrace{NH_3Hg}$. Or again, if we suppose the mercurous salts to contain, not two distinct atoms, but a *double atom* of mercury ($Hg' = Hg_2$), this double atom being the equivalent of one atom of hydrogen—thus, calomel = $Hg'Cl$; black oxide of mercury = $Hg'O$, &c., — then the ammoniacal compound, $Hg_2Cl.NH_3$ may be regarded as *chloride of mercurosammonium*, $\overbrace{NH_3Hg'}.Cl$, or chloride of ammonium in which one eq. H is replaced by a double atom of mercury.

When calomel is digested in aqueous ammonia, it turns black, and was found by Kane to be converted into *mercurous amido-chloride*, $Hg_2Cl.Hg_2NH_2$, sal-ammoniac being formed at the same time:

$$2Hg_2Cl + 2NH_3 = Hg_2Cl.Hg_2NH_2 + NH_4Cl.$$

This compound may also be regarded as *chloride of bimercurosammonium*, $\overbrace{NH_2Hg'_2}.Cl$. It is not altered by boiling water; when quite dry, it is of a grey colour.

Dibromide of mercury, Mercurous bromide, Hg_2Br, is a white insoluble powder, resembling in all respects the dichloride, and formed in similar circumstances. A boiling solution of bromide of strontium was found by Lœwig to dissolve three equivalents of dibromide of mercury, of which one equivalent precipitated during the cooling of the solution. When the filtered solution was evaporated, it deposited a salt in small crystals, containing $SrBr.2Hg_2Br$. These crystals were decomposed by pure water, and resolved into the insoluble dibromide, Hg_2Br, and a double salt, $SrBr.Hg_2Br$, which dissolved easily, and crystallized by evaporation.

Diniodide of mercury, Mercurous iodide, Hg_2I, is obtained by precipitation as a green powder, which is red when heated. It is also formed by triturating mercury and iodine together in a mortar, with a few drops of alcohol, in the proportion of 2 eq. of the former to 1 eq. of the latter.

No *dicyanide of mercury* exists; and it is doubtful whether a *difluoride*, corresponding with the dioxide, has been formed.

Mercurous carbonate, Carbonate of black oxide of mercury, $HgO_2.CO_2$, precipitates as a white powder, when an alkaline carbonate is added to the nitrate of the same oxide. The precipitate becomes grey when the liquid containing it is boiled, and carbonic acid escapes. This carbonate is soluble both in carbonic acid water, and, to a slight extent, in an excess of alkaline carbonate.

Mercurous sulphate, Sulphate of black oxide of mercury, $Hg_2O.SO_3$; 248 *or* 3100. — This salt is obtained by digesting 1 part of mercury in $1\frac{1}{2}$ parts of sulphuric acid, avoiding a high temperature, and interrupting the process as soon as all the mercury is converted into a white salt. It is also precipitated when sulphuric acid is added to a solution of mercurous nitrate. The salt may be washed with a little cold water. It crystallizes in prisms, and requires 500 times its weight of cold and 300 of hot water to dissolve it. With aqueous ammonia this salt forms a dark grey powder, containing ammonia or its elements.

Mercurous seleniate. — Aqueous solutions of seleniate of soda and mercurous nitrate form a white precipitate, probably consisting of the neutral salt, $Hg_2O.SeO_3$, which, however, gradually turns yellow during washing, and, when dried at 100°, is found to be reduced to $6Hg_2O.5SeO_3$ (Körner).

Mercurous selenite. — The neutral salt $Hg_2O.SeO_2$ is found native as *onofrite*, a yellow earthy mineral, occurring, together with horn-quicksilver and native mercury, at San Onofrio, in Mexico. It is also obtained by double decomposition as a white powder, which melts at 356°, and when heated above that point, is converted into a brick-red, opaque, crystalline mass of the salt, $3Hg_2O.4SeO_2$, (Köhler).*

Mercurous nitrates, Nitrates of black oxide of mercury. — The *neutral nitrate* is obtained when mercury is dissolved in an excess of cold nitric acid: it crystallizes readily in transparent rhombs. It is soluble with heat in a small quantity of water, but is decomposed by a large quantity of water, and an insoluble subsalt formed, unless nitric acid be added to the water. The formula of this salt is $Hg_2O.NO_5 + 2HO$. A *subnitrate* is formed when the black oxide is dissolved in a solution of the preceding salt, or when an excess of mercury is digested in diluted nitric acid at the usual temperature. It crystallizes readily in white, opaque rhombic prisms, which contain, according to both G. Mitscherlich and Kane, $3Hg_2O.2NO_5 + 3HO$; or, according to Marignac, $4Hg_2O.3NO_3 + HO$. This salt was observed by G. Mitscherlich to be dimorphous. When dissolved by dilute nitric acid, it yields the neutral salt. The subnitrate is soluble in a little water, but when treated with a large quantity, it leaves undissolved, like the neutral nitrate, a white powder, which retains its colour so long as the supernatant liquid is acid, but becomes yellow when washed with water. The *yellow subnitrate of mercury* was found to contain $2Hg_2O.NO_5 + HO$ (Kane). Another subnitrate, containing, according to Marignac, $5Hg_2O.3NO_5 + 2HO$, is obtained by boiling the solution or the mother-liquor of the neutral or the sesquibasic nitrate with excess of mercury for several hours. This salt crystallizes in colourless or slightly yellow crystals, derived from an unsymmetrical oblique prism; it appears to be the most stable of all the mercurous subnitrates. When very dilute ammonia is added to the preceding soluble nitrates, without neutralizing the whole acid, a velvety black precipitate falls, known as *Hahnemann's soluble mercury*. This salt contains, according to the analysis of C. G. Mitscherlich, $3Hg_2O.NO_5 + NH_3$. But when pains were taken to avoid decomposition of the salt in washing it, its composition was found by Kane to be $2Hg_2O.NO_5 + NH_3$. Bibasic mercurous nitrate, mixed in solution with nitrate of lead, yields a crystalline double salt, containing $2(PbO.NO_5) + 2Hg_2O.NO_5$; and similar double salts with the nitrates of baryta and strontia (G. Staedeler).

Mercurous acetate, $Hg_2O.C_4H_3O_3$, falls when acetic acid, or an acetate, is added to the nitrate, in crystalline scales of a pearly lustre. It is anhydrous, and sparingly soluble in water.

MERCURIC COMPOUNDS.

Protoxide of mercury (*red oxide*), *Mercuric oxide*, HgO, 108 *or* 1351.—This compound is formed, as described, by the oxidation of mercury at a high temperature, or by heating the nitrate of mercury till all the nitric acid is expelled, and the mass, calcined almost to redness, no longer emits vapours of nitric oxide. As prepared by the latter process, protoxide of mercury forms a brilliant orange-red powder, crystallized in plates, and having the density 11·074. It is very dark red at a high temperature, but becomes paler as it cools. When reduced to a fine powder, it becomes yellow, like litharge, without any shade of red. It was found by Mr. Donovan to be soluble to a small extent in water, forming a solution which has a slight alkaline reaction. If contaminated with nitric acid, it gives off nitrous fumes when heated in a glass tube, and forms a yellow sublimate of subnitrate. This oxide is known in pharmacy as *red precipitate*. The same compound is obtained by precipitation, when a solution of corrosive sublimate is mixed with an

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* Pogg. Ann. lxxxix. 146.

excess of caustic potash; it then forms a dense powder of a lemon-yellow colour. It is necessary to use the potash in excess, otherwise a dark brown oxychloride is formed. The precipitated oxide parts with a little moisture when gently heated, but does not change in appearance. This yellow precipitated oxide differs in some respects from the red oxide; it combines in the cold with oxalic acid, whereas the red oxide does not; it is converted into black oxychloride by the action of an alcoholic solution of mercuric chloride, which has no action on the red oxide, and it is attacked by chlorine much more readily than the latter. At a red heat, the oxide of mercury is entirely volatilized in the form of oxygen and metallic mercury; the same decomposition takes place more slowly under the influence of light. The oxide detonates when heated with sulphur, and converts chlorine into hypochlorous acid.

The salts of mercuric oxide, when they do not contain a coloured acid, are colourless in the neutral, and yellow in the basic state. They have a disagreeable metallic taste, and act as violent acrid poisons. Some of them, *e. g.*, the nitrate and sulphate, are resolved by water into a soluble acid salt, and an insoluble basic salt. From their aqueous solutions the mercury is, for the most part, precipitated in the metallic state by the same substances as from mercurous salts; but the complete reduction of the mercury is often preceded by the formation of a mercurous salt: such, for example, is the action of phosphorous acid, sulphurous acid, protochloride of tin, metallic copper, &c. *Gold* does not by itself reduce mercury from its salts; but if a drop of a mercuric solution be laid on a piece of gold, and a bar of zinc, tin, or iron be brought in contact with the moistened surface, an electrolytic action is set up, and the gold becomes amalgamated at the point of contact. *Hydrosulphuric acid* and *alkaline sulphides*, added in excess to mercuric salts, throw down a black precipitate of mercuric sulphide, insoluble in strong nitric acid. If, however, the quantity of the re-agent added is not sufficient for complete decomposition, a white precipitate is formed consisting of a compound of mercuric sulphide with the original salt, and often coloured yellow or brown by excess of the sulphide: this re-action is quite peculiar to mercuric salts. *Ammonia* and *carbonate of ammonia* form white precipitates, generally consisting of a compound of the mercuric salt with amide of mercury. The *fixed alkalies* throw down a yellow precipitate of mercuric oxide (not hydrated), insoluble in excess. If, however, the solution contains a large quantity of free acid, no red precipitate is formed, or only a slight one after a considerable time. *Monocarbonate of potash* or *soda* throws down red-brown mercuric carbonate. But if any ammoniacal salt is present in the solution, the fixed alkalies and their carbonates throw down the white precipitate above mentioned. *Bicarbonate of potash* or *soda* also gives a brown-red precipitate, with mercuric nitrate or sulphate; but with the chloride it forms a white precipitate which afterwards turns red. The *carbonates of baryta, strontia*, and *lime* precipitate mercuric oxide from the solutions of the sulphate and nitrate, but not from the chloride. *Phosphate of soda* throws down white mercuric phosphate from the sulphate and nitrate, but not from the chloride. *Chromate of potash* forms a yellowish red precipitate. *Ferrocyanide of potassium* forms, in solutions not too dilute, a white precipitate which gradually turns blue. *Tincture of galls* forms an orange-yellow precipitate with all mercuric solutions except the chloride. *Iodide of potassium* produces a scarlet precipitate of mercuric iodide, soluble in excess either of the mercuric salt or of iodide of potassium.

When aqueous ammonia is digested for several days upon precipitated oxide of mercury, the latter is converted into a yellowish white powder, which Kane regards as $2HgO.HgNH_2+3HO$, or as a hydrated compound of amide and oxide of mercury, which may be called oxyamide of mercury. According to Millon,* on the other hand, its composition is $4HgO.NH_3+2HO$, or rather $3HgO . HgNH_2.HO+2HO$.

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* Compt. rend. xxi. 826.

This substance, when placed in vacuo over quicklime, gives off 2 eq. water, turns brown, and in that state undergoes no further alteration by exposure to the air at ordinary temperatures; but between 100° and 130° C., it gives off a third atom of water, and is reduced to the anhydrous compound $3HgO . HgNH_2$. The yellow hydrated compound rapidly absorbs carbonic acid from the air, and turns white. Dilute potash has no action upon it; but very strong potash, at a boiling heat, decomposes it, with evolution of ammonia. The brown anhydrous compound resists the action of aqueous potash even at the boiling heat, but is decomposed by fusion with hydrate of potash. Oxyamide of mercury is a powerful base, and expels ammonia from its salts. One equivalent of this compound, represented by the formula $3HgO . HgNH_2$, saturates 1 eq. of sulphuric acid, nitric acid, &c.; thus the sulphate is $3HgO . HgNH_2 . SO_3$; the nitrate, $3HgO.HgNH_2.NO_5+HO$, &c. &c.

Nitride of mercury, Mercurammonia, NHg_3.—This compound is formed by passing dry ammoniacal gas over precipitated mercuric oxide previously well washed and dried:

$$3HgO+NH_3—NHg_3+3HO.$$

After removing the excess of mercuric oxide by dilute nitric acid, the mercurammonia is obtained in the form of a dark flea-brown powder, which explodes, by heat, friction, percussion, or by contact with oil of vitriol, almost as violently as iodide of nitrogen. When carefully heated with hydrate of potash, it is decomposed without detonation, yielding ammoniacal gas and sublimed metallic mercury. It is also decomposed by hydrochloric acid, sulphuric, and concentrated nitric acid, yielding an ammoniacal and a mercuric salt. It may be regarded as ammonia in which the hydrogen is entirely replaced by an equivalent quantity of mercury, (Plantamour).*

By the action of various ammoniacal salts at a boiling heat on mercuric oxide, compounds are obtained consisting of nitride of mercury combined with mercuric salts: *e. g.* with *nitrate* of ammonia, the compound $NHg_3+2(3HgO . NO_5)$ is obtained; with *phosphate* of ammonia, the compound $NHg_3+3HgO . PO_5+2HO$; with *carbonate* of ammonia, the compound $2(NHg_3+HgO . CO_2+2HO)+HO$; with *chromate* of ammonia, the compound $NHg_3 . HgO . 2HO+4(HgO.CrO_3)$, which when treated with ammonia is converted into $NHg_3+HgO . CrO_3+2HO$; with *acetate* of ammonia, the compound $NHg_3+C_4H_3HgO_4+4HO$, &c. &c. (Hirzel).†

Protosulphide of mercury, Mercuric sulphide, Cinnabar, HgS; 116 *or* 1450. —This is the common ore of mercury, and sometimes occurs crystallized, forming a beautiful vermilion. It is prepared artificially by fusing one part of sulphur in a crucible, and adding to it by degrees six or seven parts of mercury, stirring it after each addition, and covering it to preserve it from contact of air, when it inflames, from the heat evolved in the combination. The product is exposed to a sand-bath heat, to expel the sulphur uncombined with mercury, and afterwards sublimed in a glass matrass at a red heat. A brilliant red mass of a crystalline structure is thus obtained, which, when reduced to fine powder, forms the lively red pigment vermilion. This sulphide is black before sublimation. It is precipitated black also when hydrosulphuric acid is passed through a solution of corrosive sublimate, but is of the same composition in both states. The sulphide of mercury, however, may be obtained of a red colour without sublimation, or in the humid way, by several methods.

Liebig recommends for this purpose to moisten the preparation called white precipitate, recently prepared, with sulphide of ammonium, and allow them to digest together. The black sulphide is instantly produced, which in a few minutes passes into a fine red cinnabar, the colour of which is improved by digesting it at

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* Ann. Ch. Pharm. xl. 115.

† Ann. Ch. Pharm. lxxxiv. 258.

a gentle heat in a strong solution of hydrate of potash. The sulphide of ammonium used in this experiment is prepared by dissolving sulphur to saturation in hydrosulphate of ammonia. Cinnabar is not attacked by sulphuric, nitric or hydrochloric acid, or by solutions of the alkalies, but is dissolved by aqua-regia.

Protochloride of mercury, Mercuric chloride, Corrosive sublimate, 135·5 *or* 1693·75.—This compound may be formed by dissolving red oxide of mercury in hydrochloric acid, or by adding hydrochloric acid to any soluble salt of that oxide; but it is generally prepared in a different manner. Four parts of mercury are added to five parts of sulphuric acid, and the mixture boiled till it is converted into a dry saline mass. The mercuric sulphate thus obtained is mixed with an equal weight of common salt, and heated strongly in a retort by a sand-bath; chloride of mercury sublimes and condenses in the upper part and neck of the retort, while sulphate of soda remains behind with the excess of chloride of sodium. The mercury and sodium have exchanged places in the salts;

$$NaCl + HgO . SO_3 = HgCl + NaO . SO_3.$$

Mercury, when heated in a stream of chlorine gas, burns with a pale flame, and is converted into a white sublimate of chloride. The salt has been prepared on a large scale in this manner, which was suggested as a manufacturing process by Dr. A. T. Thomson.

The sublimed chloride of mercury forms a crystalline mass, the density of which is 6·5; it fuses at 509°, and boils at about 563°. The vapour of chloride of mercury is colourless, its density 9420, one volume of it containing 1 volume of mercury vapour and 1 volume of chlorine gas. This salt is soluble in 16 parts of cold and in 3 parts of boiling water, in 2½ parts of cold and in 1⅙ part of boiling alcohol, and in 3 parts of cold ether. It is not decomposed by sulphuric or nitric acid; is largely dissolved by the latter, and also by hydrochloric acid. It is obtained by sublimation and from solution in two different crystalline forms. The solutions of chloride of mercury exposed to the direct rays of the sun evolve oxygen, while hydrochloric acid is dissolved and dichloride of mercury precipitates. The decomposition of this salt by the action of light is much more rapid when the solution contains organic matter. The poisonous action of chloride of mercury, which is scarcely inferior to that of arsenious acid, is best counteracted by liquid albumen, with which chloride of mercury forms an insoluble and inert compound.

Many metals, viz. arsenic, antimony, bismuth, zinc, tin, lead, iron, nickel, and copper, decompose mercuric chloride in the dry way, withdrawing the half or the whole of its chlorine, and separating calomel or metallic mercury, which latter forms an amalgam with the excess of the other metal. Arsenic forms terchloride of arsenic and a brown sublimate. An intimate mixture of 3 pts. antimony and 1 pt. corrosive sublimate, well pressed into a glass, becomes hot and liquid in the course of half an hour, and on the application of heat yields terchloride of antimony and metallic mercury. Tin heated with corrosive sublimate yields a distillate of bichloride of tin, and a grey residue containing calomel and protochloride of tin. Many metals also reduce the mercury from the aqueous or alcoholic solution of the chloride (p. 581). Most metals throw down calomel together with the mercury; but zinc, cadmium, and iron precipitate nothing but mercury, zinc being thereby converted into a semi-fluid amalgam, and cadmium forming an amalgam which crystallizes in beautiful needles. The other reactions of mercuric chloride in solution have been already described (p. 581, 582).

Chloride of mercury with ammonia. — 1. When chloride of mercury is gently heated in a stream of ammoniacal gas, the latter is absorbed, and the compound fuses from heat evolved in the combination. The product was found by Rose to contain $2HgCl . NH_3$. This compound boils at 590°, and may be distilled without loss of ammonia; it is decomposed by water. — 2. *Fusible white precipitate.* When the double chloride of mercury and ammonium, called sal alembroth, is precipitated by potash in the cold, a white powder is obtained, which was first distinguished by Wöhler from the compound next described; its composition may be expressed, according to Kane's analysis, by the formula $HgCl.NH_3$. The same compound is also formed when ammonia is added to a solution of sal-ammoniac, the liquid brought to the boiling point, and chloride of mercury dropt into it so long as the precipitate which is produced is redissolved. The compound appears, on the cooling of the solution, in small crystals, which are garnet dodecahedrons (Mitscherlich). The crystalline form of this compound belongs, therefore, to the regular system, like that of sal-ammoniac.

3. *Mercuric amido-chloride.* — The compound known as *white precipitate*, and sometimes *infusible white precipitate*, to distinguish it from the preceding, is formed when ammonia is added to a solution of chloride of mercury. When first produced, it is bulky and milk-white; it is decomposed by hot water or by much washing with cold water, and acquires a yellow tinge. Kane has shown that white precipitate is free from oxygen, and contains nothing but the elements of a double chloride and amide of mercury, and represents it by the formula $HgCl.HgNH_2$. White precipitate is distinguished from calomel by solution of ammonia, which does not alter the former, but blackens the latter: it is readily dissolved by acids.

4. *Nitrochloride of mercury.* — Mitscherlich has observed that when white precipitate is gradually heated in a metal bath, and the heat continued for a long time, three atoms of it give off two atoms of ammonia and one atom of chloride of mercury, while a red matter remains in crystalline scales, having much the appearance of red oxide of mercury produced by the oxidation of the metal in air, and containing two atoms of chloride of mercury, united with a compound of one atom of nitrogen and three atoms of mercury, $2HgCl.NHg_3$. He concludes that the atom of white precipitate should be multiplied by three; its decomposition by the heat of the metal bath will then be represented by the equation :—

$$3(HgCl.HgNH^2) = 2HgCl.NHg_3 + 2NH_3 + HgCl.$$

The red compound is itself decomposed by a temperature above 680°, and resolved into chloride of mercury, mercury and nitrogen. It is insoluble in water, and is not altered in boiling solutions of the alkalies. It may be boiled without change in diluted or concentrated nitric acid, and in pretty concentrated sulphuric acid, but is decomposed and dissolved when boiled in the most concentrated sulphuric acid or in hydrochloric acid; no gas is evolved, but ammonia and chloride of mercury are found in the acid solution. The compound NHg_3 is not isolated by passing ammonia over the heated red compound. Mercury conducts itself in these compounds in the same way as potassium with ammonia, the olive-coloured substance produced by the action of dry ammonia upon potassium being the amide of potassium, $3(K.NH_2)$, and the plumbago-looking substance left on heating the amide of potassium, when ammonia escapes, a compound of nitrogen and potassium, NK_3.*

5. When white precipitate is boiled in water, it is changed into a heavy *canary-yellow powder*, which Kane regards as a compound of the amido-chloride of mercury with oxide of mercury, $HgCl.HgNH_2.2HgO$. Two atoms of water are decomposed in its formation, yielding the two atoms of oxygen which are found in the yellow compound, while the two atoms of hydrogen, added to an atom of chlorine and an atom of amidogen, form an atom of hydrochlorate of ammonia, which is found in solution :

$$2(HgCl.HgNH_2) + 2HO = HgCl.HgNH_2.2HgO + NH_4Cl.$$

Solutions of potash and soda convert white precipitate into the same yellow substance, while a metallic chloride is formed and ammonia evolved, (Kane).

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* Mitscherlich in Poggendorff's Annalen, vol. xxxix. p. 409.

The five compounds just described may be regarded as salts of metalloïdal radicals, formed from ammonium (NH_4) in which the whole or part of the hydrogen is replaced by an equivalent quantity of mercury. Thus, the fusible white precipitate, $HgCl.NH_3$, may be regarded as a *chloride of mercurammonium*, $= Cl.N\left\{\begin{matrix}H_3\\Hg\end{matrix}\right.$; the preceding compound, $2HgCl.NH_3$, as a double chloride consisting of the same compound united with chloride of mercury, namely as $ClHg + Cl.N\left\{\begin{matrix}H_3\\Hg\end{matrix}\right.$; similarly, infusible white precipitate, $HgCl.HgNH_2$, is a *chloride of bimercurammonium*, $ClN\left\{\begin{matrix}H_2\\Hg_2\end{matrix}\right.$; the yellow powder obtained by boiling this compound with water is a *chloride of tetramercurammonium* combined with two atoms of water, $= ClNHg_4 + 2HO$; and the red compound, $2HgCl.NHg_3$, may be regarded as a compound of this same chloride with chloride of mercury, namely as $ClHg.ClNHg_4$.

Oxychloride of mercury. — When a solution of corrosive sublimate is precipitated by potash or soda, mercuric oxide goes down, in combination with a portion of chloride, as a brown precipitate, unless a considerable excess of alkali be employed. The same oxychloride is produced by an alkaline carbonate; but a double carbonate is then also formed. Chloride of mercury is not immediately precipitated by the bicarbonates of potash and soda; and hence that salt may be employed to detect the presence of a neutral alkaline carbonate in these bicarbonates. This oxychloride may also be formed by passing chlorine through a mixture of water and oxide of mercury. It may be obtained crystalline and of a very dark colour, almost black, by mixing corrosive sublimate with chloride of lime, and boiling the liquid, or by treating a solution of corrosive sublimate with bicarbonate of potash, and allowing the solution to stand in an open vessel, when carbonic acid gradually escapes, and the compound $HgCl.4HgO$ is deposited. This oxychloride is decomposed by a moderate heat, chloride of mercury subliming, while the red oxide remains.

Sulphochloride of mercury, $HgCl.2HgS$. — When hydrosulphuric acid gas is passed through a solution of chloride of mercury, the precipitate which first appears, and does not subside readily, is white; it has been shown by Rose to be a compound of chloride and sulphide of mercury. This substance is changed entirely into sulphide of mercury, when left in water containing hydrosulphuric acid. On the other hand, precipitated sulphide of mercury digested in a solution of chloride of mercury, takes down that salt, and forms the compound in question. The same compound may be formed in the dry way, by fusing protosulphide of mercury (either black or red) with eight or ten times its weight of corrosive sublimate, in a sealed tube, and dissolving out the excess of chloride by boiling water; the sulphochloride then remains *in the form of a dirty-white powder* having a distinctly crystalline structure (R. Schneider). Sulphide of mercury combines likewise with the bromide, iodide, fluoride, and nitrate of mercury, and always in the proportion of two atoms of the sulphide to one atom of the other salt.

Double salts of chloride of mercury. — Chloride of mercury was found by M. Bonsdorff to combine with *chloride of potassium* in three different proportions, forming a series of salts in which the chloride of potassium remains as one equivalent, while the chloride of mercury goes on increasing. They are $KCl.HgCl.HO$, which crystallizes in large transparent rhomboidal prisms; $KCl.2HgCl.2HO$ crystallizing in fine needle-like amianths; and $KCl+4HgCl+4HO$, which crystallizes also in fine needles. *Chloride of sodium* forms only one compound, $NaCl.2HgCl.4HO$, which crystallizes in fine regular hexahedral prisms. One of the double salts of *chloride of ammonium* has long been known as *sal alembroth.* It crystallizes in flattened rhomboidal prisms, $NH_4Cl.HgCl.HO$, and is isomorphous with the corresponding potassium salt. When exposed to dry air, it gives off its water without change of form. Kane has also obtained $NH_4Cl.2HgCl$, and the same with an atom of water, $NH_4Cl.2HgCl.HO$, the first in a rhomboidal form, and the second in long silky needles. All these double chlorides are obtained by dissolving their constituent salts together in the proper proportions. The *chlorides of barium* and *strontium* form well-crystallized compounds with *chloride of mercury*, viz. $BaCl.2HgCl.4HO$, and $SrCl.2HgCl.2HO$. *Chloride of calcium* combines in two proportions with mercuric chloride. When chloride of mercury is dissolved to saturation in chloride of calcium, tetrahedral crystals separate from the solution, which are tolerably persistent in air, and contain $CaCl.5HgCl.8HO$. After the deposition of these crystals, the liquid yields, when evaporated by a gentle heat, a second crop of large prismatic crystals, $CaCl.2HgCl.6HO$, which are very deliquescent. *Chloride of magnesium* also forms two salts, $MgCl.3HgCl.HO$, and $MgCl.HgCl.6HO$, both deliquescent. *Chloride of nickel* gives two compounds, one of which crystallizes in tetrahedrons, like the chloride of calcium salt. *Chloride of manganese* forms a compound in good crystals, $MnCl.HgCl.4HO$. The *chlorides of iron* and *zinc* form similar isomorphous salts, $FeCl.HgCl.HO$, and $ZnCl.HgCl.HO$. The double chlorides of zinc and of manganese are remarkable in one respect, that chloride of mercury dissolved by them in excess crystallizes by evaporation in fine large crystals, such as cannot be obtained in any other way. The *chlorides of cobalt, nickel,* and *copper* form similar crystallizable salts; but chloride of lead does not appear to form a double salt with chloride of mercury. (Bonsdorff.)

Mercuric chloride likewise forms definite compounds with *alkaline chromates.* A hot solution of equal parts of mercuric chloride and *bichromate of ammonia* deposits, on cooling, large hexagonal prisms, of a splendid red colour, containing $NH_4O.2CrO_3+HgCl+HO$, and the mother-liquor deposits a further crop of red, somewhat needle-shaped crystals, containing $3(NH_4O.2CrO_3)+HgCl$. (Richmond and Abel.*) *Monochromate of potash* forms with mercuric chloride a brick-red precipitate of mercuric chromate; and, on evaporating the filtered liquid, small pale red crystals are obtained of a double salt, containing $KO.CrO_3+HgCl$. A solution of equivalent quantities of mercuric chloride and *bichromate of potash* yields beautiful red pointed crystals, containing $KO.2CrO_3+HgCl$. (Darby.†) On mixing the cold saturated aqueous solutions of *acetate of copper* and mercuric chloride, and leaving the mixture to evaporate, deep blue, concentric, radiated hemispheres are obtained, containing $CuO.C_4H_3CuO_4+HgCl$. (Wöhler and Hütteroth.)‡

Protobromide of mercury, Mercuric bromide, $HgBr$; 180 or 2250.—This salt is obtained by treating mercury with water and bromine. It is colourless, soluble in water and alcohol, and when heated, fuses and sublimes, exhibiting a great analogy to chloride of mercury in its properties. Its density in the state of vapour is 12370. Bromide of mercury forms a similar compound with sulphide of mercury, $HgBr.2HgS$, which is yellowish. It was also combined, by Bonsdorff, with a variety of alkaline and earthy bromides. Bromide of mercury combines with half an equivalent of ammonia, in the dry way, and also gives, with solution of ammonia, a white precipitate, analogous to that derived from chloride of mercury.

Protiodide of mercury, mercuric iodide, HgI, 226·36 *or* 2829·5.—Falls as a precipitate of a fine scarlet colour, when iodide of potassium is added to a solution of chloride of mercury. It may also be obtained by triturating its constituents together, in the proper proportion, with a few drops of alcohol. To procure it in crystals, Mitscherlich dissolves iodide of mercury to saturation, in a hot concentrated solution of the iodide of potassium and mercury, and allows the solution to cool gradually. When heated moderately, mercuric iodide becomes

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* Chem. Soc. Qu. J. iii. 202.

† Chem. Soc. Qu. J. i. 24.

‡ Ann. Ch. Pharm. liii. 142.

yellow; at a higher temperature, it fuses and sublimes, condensing in rhomboidal plates of a fine yellow colour. The forms of the red and yellow crystals are totally different, so that the change of colour is due to the dimorphism of mercuric iodide. The yellow crystals generally return gradually into the red state when cold; and this change may be determined at once by scratching the surface of a crystal, or by crushing it. The density of mercuric iodide in the state of vapour is 15630; it is the heaviest of gaseous bodies. Mercuric iodide is slightly soluble in water, but requires more than 6000 times its weight of water to dissolve it. It is much more soluble in alcohol and in acids, particularly with the assistance of heat. Mercuric iodide is very soluble in iodide of potassium; it is also dissolved by a solution of mercuric chloride, especially when hot. Hence, when a few drops of iodide of potassium solution are added to a solution of corrosive sublimate, a precipitate is formed, which redissolves on agitating the liquid; a somewhat larger quantity of iodide of potassium renders the precipitate permanent; and a still further addition causes it to disappear entirely.

When treated with sulphuretted hydrogen water, mercuric iodide forms the compound $HgI.2HgS$, which is yellow. Mercuric iodide unites with other iodides, and forms a class of salts as extensive as the compounds of chloride of mercury. They have been studied by M. P. Boullay.[*] Mercuric iodide also combines with chlorides; it is dissolved by a hot solution of mercuric chloride, and two compounds have been obtained on the cooling of the solution, viz., a yellow powder, $HgI.HgCl$, and white dendritic crystals, $HgI.2HgCl$.

Mercuric iodide treated with very strong aqueous ammonia forms the compound $N\overbrace{H_3Hg}.I$; with somewhat less concentrated ammonia it yields white needles of the compound $NH_3.2HgI$, or $N\overbrace{H_3Hg}I + HgI$, and a red-brown powder consisting of iodide of tetramercurammonium with 2 eq. water, $NHg_4I + 2HO$. The formation of this last compound is represented by the equation:

$$4HgI + 4NH_3 + 2HO = NHg_4I.2HO + 3NH_4I.$$

Iodide of tetramercurammonium is also formed by passing ammoniacal gas over mercuric oxy-iodide:

$$HgI.3HgO + NH_3 = NHg_4I.2HO + HO;$$

by digesting the chloride of tetramercurammonium in aqueous iodide of potassium (Rammelsberg); and by adding ammonia to a solution of iodide of mercury and potassium mixed with caustic potash (Nessler):[†]

$$4(HgI.KI) + NH_3 + 3KO = NHg_4I.2HO + 7KI + HO.$$

This last reaction affords an extremely delicate test for ammonia. A solution of iodide of mercury and potassium is prepared by adding iodide of potassium to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is re-dissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained produces a brown precipitate with a very small quantity of ammonia, either free or in the form of an ammoniacal salt. The precipitate is soluble in excess of iodide of potassium (Nessler).

Mercuroso-mercuric iodide, Hg_4I_3 *or* $Hg_2I.2HgI$. — This compound is obtained by precipitating a solution of mercurous nitrate with hydriodic acid or iodide of potassium, and collecting the precipitate on a filter after the green colour has changed to yellow; or by dissolving in aqueous iodide of potassium half as much iodine as it already contains, and adding the solution to a solution of mercurous nitrate. It is a yellow powder, which turns red when heated.

Cyanide of mercury, $HgCy$, 126 *or* 1575.—This salt is most easily obtained by

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[*] Ann. Ch. Phys. [2.] xxxiv. 337.

[†] Chem. Gaz. 1856, 445, 463.

saturating hydrocyanic acid with red oxide of mercury. To prepare the hydrocyanic acid required, the process of Winkler may be followed. Fifteen parts of ferrocyanide of potassium are distilled with 13 parts of oil of vitriol diluted with 100 parts of water, and the distillation continued by a moderate heat nearly to dryness. The vapour should be made to pass through a Liebig's condensing tube, and be afterwards received in a flask containing 30 parts of water. A portion of the condensed hydrocyanic acid is put aside, and the remainder mixed with 16 parts of oxide of mercury in fine powder, and well agitated till the odour of hydrocyanic acid is no longer perceptible. The solution is drawn off from the undissolved oxide of mercury, and the reserved portion of hydrocyanic acid mixed with it. The last addition is necessary to saturate a portion of oxide of mercury, which cyanide of mercury dissolves in excess. This operation yields 12 parts of the salt in question.

Cyanide of mercury may also be obtained by boiling 1 pt. of ferrocyanide of potassium for ten minutes with 2 pts. of neutral mercuric sulphate and 8 pts. of water, filtering the liquid, and leaving it to crystallize by cooling. The reaction may be represented by the equation:

$$K_2FeCy_3 + 3HgO = 3HgCy + 2KO + FeO.$$

A third method of preparing this compound is to heat the red oxide of mercury with about an equal weight of pure and finely powdered Prussian blue, and a large quantity of water, stirring the mixture frequently; then boil the filtrate with oxide of mercury to throw down the last portions of iron; and neutralize the excess of mercuric oxide in the liquid with hydrocyanic acid.

Cyanide of mercury crystallizes in square prisms, which are anhydrous, and resembles chloride of mercury in its solubility and poisonous qualities. The red oxide of mercury, even when dry, absorbs hydrocyanic acid, with formation of water and evolution of heat. The affinity of mercury for cyanogen appears to be particularly intense, oxide of mercury decomposing all the cyanides, even cyanide of potassium, and liberating potash. Cyanide of mercury is consequently not precipitated by potash. Nor is it decomposed by any acid, with the exception of hydrochloric, hydriodic, and hydrosulphuric acids. By a heat approaching to redness, cyanide of mercury is decomposed, and resolved into mercury and cyanogen gas. When exposed in the moist state to the action of chlorine in a dark place, it is converted into mercuric chloride and gaseous chloride of cyanogen:

$$HgCy + 2Cl = HgCl + CyCl.$$

But in strong sunshine, a different action takes place, attended with considerable rise of temperature, and yielding sal-ammoniac, mercuric chloride, a peculiar yellow oil, a small quantity of gaseous chloride of cyanogen, and a trace of carbonic acid (Serullas). When hydrocyanic acid is digested upon mercurous oxide, the mercuric cyanide dissolves, and metallic mercury is liberated.

Oxycyanide of mercury, $HgCy.HgO$, is produced as a white powder intermixed with the red oxide, when hydrocyanic acid of considerable strength (10 or 20 per cent.) is agitated with red oxide of mercury in large excess. It is sparingly soluble in cold water, but may be dissolved out by hot water, and crystallizes on cooling in transparent, four-sided, acicular prisms. When heated gently, it blackens slightly, and then explodes (Johnston).*

Cyanide of mercury, digested upon red oxide of mercury, dissolves a large quantity of it, and forms, according to Kühn, a *tribasic cyanide of mercury*, $HgCy.3HgO$, which is more soluble in water than the neutral cyanide, and crystallizes with less facility in small acicular crystals.

Cyanide of mercury and potassium, $KyCy.HgCy$, is formed on dissolving cyanide of mercury in a solution of cyanide of potassium, and crystallizes in regular

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* Phil. Trans. 1839, p. 113.

octohedrons. Cyanide of mercury also forms crystallizable double salts with other cyanides, such as the cyanides of sodium, barium, calcium, magnesium, &c. It also combines with chlorides, bromides, iodides, and with several oxi-salts, such as chromate and formiate of potash, with which it forms the compounds $2(KO.CrO_3)+HgCy$ and $C_2HKO_4.HgCy$.

Mercuric sulphate, $HgO.SO_3$; 148 *or* 1850. — This salt is formed by boiling 5 parts of sulphuric acid upon 4 parts of mercury, till the metal is converted into a dry saline mass. Mercuric sulphate is a white crystalline salt, neutral in composition, but, like most of the neutral salts of mercury, cannot exist in solution. Water decomposes it, forming a dense yellow subsulphate, and a solution of an acid sulphate. This subsulphate is known as *turbith mineral*, a name applied to it by the older chemists, because it was supposed to produce effects in medicine analogous to those of a root formerly employed, and known as convolvulus turpethum. The composition of turbith mineral is $3HO.SO_3$ or $HgO.SO_3 + 2HgO$ (Kane). Solution of ammonia converts both the neutral sulphate and turbith mineral into a heavy powder, which Kane names *ammonio-turbith*, and finds to be $HgO.SO_3 + Hg.NH_2 + 2HgO$. It is, therefore, analogous in composition to the yellow powder produced by the decomposition of white precipitate, and may be regarded as a sulphate of tetramercurammonium with 2 eq. of water: $NHg_4.SO_4 + 2HO$.

Mercuric sulphites. — The neutral sulphite, $HgO.SO_2$, may be formed by precipitating the nitrate, $HgO.NO_5$, with an alkaline sulphate; but it is very unstable, and resolves itself spontaneously into mercuric sulphate and metallic mercury. The *basic sulphite*, $2HgO.SO_2$, is obtained by precipitating a solution of the basic nitrate, $2HgO.SO_5$, with an alkaline sulphite. It is a white, heavy powder, insoluble in water, and changing, when slightly heated, into mercurous sulphate; $2HgO.SO_2 = Hg_2O.SO_3$. Iodide of potassium converts it into red mercuric iodide (Péan de St. Gilles).* A *bisulphite*, $HgO.2SO_2 + HO$, is obtained as a white crystalline powder by pouring a saturated solution of bisulphite of soda on solid mercuric chloride. It dissolves readily in water, and is decomposed by heat, whether in solution or in the solid state, with separation of metallic mercury (Wicke).† By treating mercuric chloride with a solution of neutral sulphite of potash, a double salt, $HgO.SO_2 + HO$, is obtained in small needle-shaped crystals, whose solution is neutral to test-paper. Similar salts are formed with the neutral sulphites of soda and ammonia. By treating mercuric chloride in excess with neutral sulphite of soda, the salt, $2(HgO.SO_2) + NaO.SO_2 + HO$, is obtained, which is alkaline to test-paper. The solutions of these double sulphites are precipitated by hydrosulphuric acid and soluble sulphides, but not by alkalies. (Péan de St. Gilles).

Mercuric seleniate.—A hot aqueous solution of selenic acid forms with mercuric oxide prepared by precipitation, a soluble neutral seleniate, $HgO.SeO_3 + HO$, and a red insoluble basic salt, containing $2(3HgO.SeO_3) + HO$ (Körner).‡

Mercuric selenite.—Mercuric oxide forms with aqueous selenious acid, according to Berzelius, an insoluble neutral and a soluble acid selenite; according to Köhler, on the other hand, selenious acid does not form any soluble salt with mercuric oxide, but only a pale yellow amorphous salt, containing $7HgO.4SeO_2$.

Nitrates of the red oxide of mercury, Mercuric nitrates. — The neutral nitrate cannot be crystallized, but it is formed in solution when chloride of mercury is precipitated by nitrate of silver. When red oxide of mercury is dissolved in nitric acid, or when the metal is dissolved in the same acid with ebullition, till a drop of the solution no longer occasions a precipitate in water containing a soluble chloride, a subnitrate is formed, crystallizing in small prisms, which are deliquescent in damp air. Its composition is expressed by the formula $2HgO.NO_5 + 2HO$.

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* Ann. Ch. Phys. [3], xxxvi. 80.

† Ann. Ch. Pharm. xcv. 176.

‡ Pogg. Ann. lxxxix. 446.

It is the only crystallizable nitrate of this oxide. Decomposed by water, this salt yields a yellow subnitrate, which, after washing with warm, but not boiling water, is $3Hg.NO_5 + HO$. When the sub-nitrate is prepared by boiling water, it has a red colour, and probably consists of $6HgO.NO_5$, (Kane).

Nitrate of mercury yields several compounds when treated with ammonia. (*a.*) When a dilute and not very acid solution of that salt is treated in the cold, with weak solution of ammonia not added in excess, a pure milk-white precipitate appears, which is not granular, and remains suspended in the liquid for a considerable time. It was analyzed by C. G. Mitscherlich, and to distinguish it from some other salts containing the same constituents, may be called *Mitscherlich's ammonia-subnitrate.* It contains $2HgO.NO_5 + HgNH_2$. (*b.*) The preceding compound is altered in its appearance by boiling water, and becomes much heavier and more granular, forming *Soubeiran's ammonia-subnitrate,* the composition of which is found by Kane to be $HgO.NO_5 + Hg.NH_2 + 2HgO$, or it resembles in constitution the bodies already described containing chlorine and sulphuric acid. This compound is also formed by decomposing a dilute solution of mercuric nitrate with a slight excess of ammonia (Soubeiran). (*c.*) A third compound, the *yellow crystalline ammonia-subnitrate,* was obtained by C. G. Mitscherlich by boiling the ammonia subnitrate (*a*) with excess of ammonia, and adding nitrate of ammonia, by which a portion of the powder is dissolved; the solution, as it cools and loses ammonia, yields small crystalline plates of a pale yellow colour. The constituents of this salt are $2HgO.NO_5$ and NH_3. Kane doubles its equivalent, and represents it as a compound of Soubeiran's salt with nitrate of ammonia, as it appears to be produced by the solution of the former salt in the latter, $(HgO.NO_5 + Hg.NH_2 + HgO) + NH_4O.NO_5$. (*d.*) Soubeiran's ammonia subnitrate (*a*) is dissolved in considerable quantity, when boiled in a strong solution of nitrate of ammonia, and the solution deposits, on cooling, small but very brilliant needles, which were observed and analyzed by Kane. This salt, which may be called *Kane's ammonia subnitrate,* is decomposed by water, nitrate of ammonia dissolving, and Soubeiran's subsalt being left undissolved. It contains the elements of $3(NH_4O.NO_5)$ and $4HgO$. Kane believes that it is most likely to contain Soubeiran's subnitrate ready formed, which leaves two atoms of nitrate of ammonia and two atoms of water to be otherwise disposed of.*

These ammonia-nitrates, like the corresponding chlorides and sulphates, may be regarded as nitrates of mercurammoniums, containing one or more atoms of mercury in place of hydrogen. Thus, Mitscherlich's ammonia-subnitrate (*a*) is $N\overbrace{HHg_3}.NO_6 + HO$ = nitrate of trimercurammonium with 1 eq. water; Soubeiran's salt (*b*) is $NHg_4.NO_6 + 2HO$ = nitrate of tetramercurammonium with 2 eq. water; the crystalline salt (*c*) is $N\overbrace{H_2Hg_2}.NO_6 + HO$ = nitrate of bimercurammonium with 1 eq. water; and (*d*) is a compound of (*b*) with nitrate of ammonia and water $= 2(NH_4.NO_6) + 2HO + (NHg_4.NO_6 + 2HO)$.

Nitrate of mercury forms an insoluble compound with sulphide of mercury $HgO.NO_5 + 2HgS$, resembling the compounds of the sulphate and chloride with sulphide of mercury. It also forms double salts with iodide and cyanide of mercury.

Alloys of mercury or amalgams. — Mercury combines with a great number of metals, forming compounds called *amalgams,* which are liquid or solid according as the mercury or the other metal predominates. A very small quantity of a foreign metal suffices to impair the fluidity of mercury in a very great degree. All amalgams are decomposed by heat, the mercury volatilizing and the other metal remaining.

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* Trans. of the Royal Irish Academy, vol. xix. pt. i.; or, Ann. Ch. Phys. [2], lxxxii. 225.

The union of mercury with potassium and sodium is attended with considerable disengagement of heat; the resulting amalgams are of a pasty consistence, and decompose water. The amalgams of tin and lead, when heated till they are quite liquid, and then left to cool slowly, yield solid crystalline amalgams of definite constitution. An amalgam of silver, Hg_2Ag, is found native in the form of regular dodecahedrons.

An amalgam of tin is used for *silvering* glass. For this purpose a sheet of tinfoil is laid on a horizontal table, and mercury poured over the whole surface, so as to form a layer about 1-5th or 1-6th of an inch thick. The plate of glass is then slid along the surface in such a manner as to cut this layer in halves horizontally, which prevents the introduction of air-bubbles. The glass is then loaded with weights, so as to press out the excess of mercury; and after a few days, the surface is found to be covered with a closely-adhering layer of an amalgam containing about 5 parts of tin to 1 of mercury.

Mercury combines very readily with bismuth. An amalgam obtained by heating a mixture of 497 parts of bismuth, 310 lead, 177 tin, and 100 mercury, is very well adapted for injecting anatomical preparations: it is solid at ordinary temperatures, and has a silvery lustre, melts at 171·5 (Fah.), and solidifies at 140°. An amalgam of lead and tin, sometimes also containing bismuth, is used for covering the cushions of electrical machines.

ESTIMATION OF MERCURY, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS,

Mercury is generally estimated in the metallic state; sometimes, however, as sulphide, HgS, or as dichloride, Hg_2Cl. To separate it from its compounds in the metallic state, it may be distilled with quicklime, in a tube of hard glass sealed at one end. Into this tube is introduced, first a layer of carbonate of lime, about an inch long; then the mixture of the substance with quicklime; lastly, a layer of quicklime about two inches long, and a plug of asbestos to keep the lime in its place. The open end of the tube is next drawn out into a narrow neck, and bent at an obtuse angle. The tube is laid in a combustion-furnace, the same as that which is used for organic analysis (277), the neck being turned downwards and made to pass into a narrow-mouthed bottle containing water, so as to terminate just above the surface of the water. The tube is then gradually heated by laying pieces of red-hot charcoal round it, beginning at the part near the neck, containing the pure quicklime. This portion having been brought to a full red heat, the heat is carefully extended towards the middle part, to decompose the compound and volatilize the mercury: any portion of the compound that may volatilize undecomposed, will be decomposed in passing over the red-hot lime at the end. Lastly, the back part of the tube containing the carbonate is heated, so as to evolve carbonic acid gas and sweep out all the mercury vapour contained in the tube. The quantity of carbonic acid thus evolved may be increased by mixing the carbonate of lime with bicarbonate of soda. The mercury condenses under the water in the bottle, which must be kept cold. The water is poured off as completely as possible; the mercury transferred to a weighed porcelain crucible; the greater part of the water which still adheres to it removed by means of blotting-paper; the drying completed over sulphuric acid; and the mercury finally weighed.

Mercury may also be precipitated from its solutions in the metallic state by protochloride of tin, or by phosphorous acid; the solution then decanted; the mercury washed with water; and dried in the manner just described.

Mercury is also frequently precipitated from its solutions, as a sulphide, by hydrosulphuric acid. In that case, if the precipitate consists of the pure protosulphide, HgS, as when it is thrown down from a solution of corrosive sublimate, the precipitate may be simply collected on a weighed filter, washed, dried over the water-bath, weighed, and the quantity of mercury thence determined. But if, as is generally the case, the precipitate also contains free sulphur, as when it is thrown down from a solution containing a ferric salt, or a considerable excess of nitric acid,—or if it be precipitated in conjunction with the sulphides of other metals, then the mercury must be separated from it by distillation with lime, as above described. Or again, the mixture of sulphides may be converted into chlorides by gentle heating in a stream of chlorine gas, the volatile chloride of mercury passed into water, and the mercury precipitated from the solution by protochloride of tin.

The precipitation of mercury in the form of dichloride is best effected by means of hydrochloric acid and forminate of potash or soda. If the mercury is contained in an alloy, the alloy must be dissolved in aqua-regia; if it is contained in solution in the form of mercuric nitrate, hydrochloric acid must be added, the solution, in either case, nearly neutralized with potash, forminate of potash or soda then added, and the whole exposed for some days to a temperature between 140° and 176° F. (at the boiling heat, the mercury would be reduced to the metallic state). The dichloride then precipitates, and must be collected on a weighed filter, washed, dried at a gentle heat, and weighed.

The quantity of *mercurous oxide* present in a solution may also be determined by precipitation with hydrochloric acid. The solution must, however, be very dilute, and be kept cool; it must also contain but a very small quantity of free nitric acid, as a larger quantity would convert the dichloride of mercury into protochloride. To determine the proportions of mercurous and mercuric oxide, when they exist together in solution, the mercurous oxide is first precipitated with hydrochloric acid, and the remaining mercury by protochloride of tin or hydrosulphuric acid.

Mercury may be separated from all other metals, except arsenic and antimony, by its superior volatility. When it exists in the form of an amalgam, the compound is simply heated, and the quantity of mercury determined by the loss of weight. If it exists as an oxide, chloride, &c., combined with compounds of other metals, it may be separated by distillation with quicklime, as above described. Its separation from the *alkalies* and *earths*, and from *uranium*, *manganese*, *nickel*, *cobalt*, *iron*, *zinc*, and *chromium*, may also be effected by precipitation with hydrosulphuric acid. From *bismuth* and *cadmium* it may be separated by reduction with protochloride of tin; from *copper*, by mixing the solution with excess of cyanide of potassium, and passing hydrosulphuric acid through the liquid, whereby the mercury is precipitated as sulphide, while the copper remains dissolved; from *lead*, by precipitating that metal with sulphuric acid; also by treating the solution with excess of cyanide of potassium, which precipitates the lead, but not the mercury. From *arsenic*, *tin* and *antimony*, mercury is separated by the solubility of the sulphides of metals in sulphide of ammonium.

SECTION II.

SILVER.

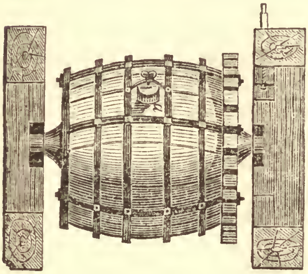
Eq. 108, *or* 1350; Ag (*argentum*).

This metal is found in various parts of the world, and occurring often in the metallic state, and being easily melted, must have attracted the attention of mankind at an early period. Before the discovery of America, the silver mines of Saxony were of considerable importance; but the silver mines of Mexico and Peru far exceed in value the whole of the European and Asiatic mines, the former having furnished during the last three centuries, according to Humboldt, 316 millions of pounds troy of pure silver.

A considerable quantity of silver is obtained from ores of lead by cupellation, as described under that metal. From argentiferous copper ores also the silver is extracted by a process called *liquation*, which consists in fusing the *coarse copper* (p. 476) with three times its weight of lead; a mixture of two alloys is then obtained, the more fusible of which, containing the greater part of the lead and nearly all the silver, is separated by the application of a moderate heat, and yields the silver by cupellation.

Native silver, which is in the form of threads or thin leaves, is separated from the gangue or accompanying rock, by *amalgamation*, a process which is also followed in the treatment of the most frequent ore of silver, the sulphide, when it is not accompanied by sulphide of lead. At Freiburg, in Saxony, the sulphide of silver, ground to powder, is roasted in a reverberatory furnace with 10 per cent. of chloride of sodium, by which the silver is converted into chloride. It is then introduced into barrels (fig. 204), with water, iron, and a quantity of metallic mercury, and the materials kept in a state of agitation for eighteen hours by the revolution of the barrels on their axes. The chloride of silver, although insoluble, is reduced to the metallic state by the iron, and chloride of iron is produced, while the silver forms a fluid compound with the mercury. By adding more water, and turning the barrels more slowly, the fluid amalgam separates and subsides. It is drawn off and subjected to pressure in a chamois leather bag, the mercury passing through the leather, while a soft amalgam of silver remains in the bag. The mercury is afterwards separated from this amalgam by a species of distillation, *per descensum*, and the silver remains.

FIG. 204.



In South America, where fuel is scarce, a different process is adopted. The ore, in a finely divided and moist condition, is exposed for a considerable time to the successive action of common salt, sulphate of copper (obtained by roasting copper pyrites), and mercury, the materials being spread on a paved floor, and trodden by men or horses to effect an intimate mixture; and the silver amalgam thus obtained is separated from the exhausted ore by washing with water. In this process, the chloride of sodium and sulphate of copper form sulphate of soda and protochloride of copper. The latter gives up chlorine, converting part of the silver into chloride, and separates the sulphur, provided an excess of chloride of sodium is present to dissolve the dichloride of copper as it forms. The dichloride of copper then acts upon another portion of the sulphide of silver, forming disulphide of copper and chloride of silver: $Cu^2Cl + AgS = Cu^2S + AgCl$. The chloride of silver thus produced, dissolves in the chloride of sodium, and is decomposed by the mercury subsequently added, yielding calomel and metallic silver. This process is always attended with considerable loss of mercury, which however may be diminished by the previous addition of iron. Mr. P. Johnston proposes to diminish the loss of mercury, as soluble chloride, which occurs in this process, by using an amalgam of zinc and mercury, instead of pure mercury.

Silver is obtained free from other metals, and in a state of purity, for chemical and other purposes, by the following processes:— 1. The metal is dissolved in pure nitric acid slightly diluted, and precipitated by a solution of chloride of sodium, the salts of the other metals present remaining in solution. The insoluble chloride of silver, thus obtained, is thoroughly washed upon a filter with hot water and dried. A quantity of carbonate of potash, equal to twice the weight of the silver, is then fused in a crucible, and the chloride of silver gradually added to it, whereupon chloride of potassium is formed, and carbonic acid and oxygen escape with effervescence. The crucible is then exposed to a heat sufficient to fuse the reduced silver, which subsides to the bottom.—2. The mode of separating silver from the common metals, in the ordinary practice of assaying, is, like many metallurgic operations, an exceedingly elegant and refined process. A portion of the silver alloy, the *assay*, is fused with several times its weight of pure lead (an alloy of 1 copper and 15 silver with 96 lead, for instance) upon a bone-earth cupel, which is supported in a little oven or muffle, heated by a proper furnace. Air being allowed access to the assay, the lead is rapidly oxidated, and its highly fusible oxide imbibed, as it is produced, by the porous cupel. The disposition of copper and other common metals to oxidate is increased by the presence of the lead; and their oxides, which form fusible compounds with oxide of lead, are removed in company with the latter. When the foreign metal is almost entirely removed, the assay is observed to become rounder and more brilliant, and the last trace of fused oxide occasions a beautiful play of prismatic colours upon its surface, after which the assay becomes, in an instant, much whiter, or *flashes*, an indication that the cupellation is completed.

Pure silver may also be obtained from an alloy containing only silver and copper, by precipitating the two metals with excess of carbonate of soda with the aid of heat, boiling the precipitate for about ten minutes with a solution of grape-sugar, whereby the copper is reduced to the state of red oxide, and the silver to the metallic state, and treating the moist precipitate with a hot solution of carbonate of ammonia: the copper then dissolves, and pure silver remains.

Pure silver is the whitest of the metals, and susceptible of the highest polish; when granulated by being poured from a height of a few feet into water, its surface is rough, but its aspect peculiarly beautiful. It crystallizes in cubes and regular octohedrons, both from a state of fusion and by precipitation from solution. Silver is in the highest degree ductile and malleable; its density varies between 10·474 and 10·542; it fuses at 1873°. When in the liquid state, it is capable of absorbing oxygen gas from the air, which is discharged again in the solidification of the metal, and gives rise to a sort of vegetation upon its surface, or even occasions the projection of small portions of the silver to a distance, an accident which is known in assaying as the *spitting* of the metal. Gay-Lussac observed, that when a little nitre was thrown upon the surface of melted silver in a crucible, and the whole kept in a state of fusion for half an hour, a very considerable absorption of oxygen took place. When the crucible was removed from the fire and quickly placed under a bell-jar filled with water, which can be done without danger, the silver discharged a quantity of oxygen equal to 20 times its volume. This property is possessed only by pure silver, and does not appear at all in silver containing 1 or 2 per cent. of copper. As oxide of silver is reduced by a red heat, the absorption of the oxygen by the fluid metal must be a phenomenon of a different nature from simple oxidation.

Silver does not combine with the oxygen of the air at the usual temperature, nor even when heated; the tarnishing of polished silver in air is occasioned by the formation of sulphide of silver. Silver does not dissolve in any hydrated acid, by substitution for hydrogen, but on the contrary is displaced from solution in an acid by hydrogen, and precipitated in the metallic state. This metal is also precipitated by mercury and by all the more oxidable metals. Its salts are reduced at the usual temperature by sulphate of iron, the protoxide in which is converted into sesquioxide. But if the ferric sulphate is boiled upon the precipitated silver, the latter is dissolved again, and oxide of silver and protoxide of iron reproduced. Silver, however, is oxidated when fused or heated strongly in contact with substances for which oxide of silver has a great affinity, as with a siliceous glass, and stains the glass yellow. It is oxidated by concentrated sulphuric acid, with evolution of sulphurous acid. Silver is readily dissolved by nitric acid, at a gentle heat, and with much violence, at a high temperature, nitrate of silver being formed, and nitric oxide escaping. Silver combines in three proportions with oxygen, forming a suboxide, Ag_2O, a protoxide AgO, and a peroxide, AgO_2.

Suboxide of silver, Ag_2O.—Pure protoxide of silver is completely reduced to the state of metal by hydrogen gas, at 212°; but the oxide contained in citrate of silver loses only half its oxygen under the same circumstances, the suboxide being formed, and remaining in combination with one half of the citric acid of the former salt. The aqueous solution of the suboxide salt is dark brown, and the suboxide is precipitated black from it by potash. When the solution of the subsalt is heated, it becomes colourless, and metallic silver appears in it. The salt dissolves with a brown colour in ammonia. Several other salts of silver, containing organic acids, comport themselves in the same way as the citrate, when heated in hydrogen.* A solution of protoxide of silver in ammonia deposits on exposure to the air, a grey suboxide, containing 108 parts of silver to 5·4 parts oxygen. When heated, it gives off oxygen and leaves metallic silver (Faraday).†

Protoxide of silver, AgO, 116 *or* 1450.—This oxide is thrown down, when potash or lime-water is added to a solution of nitrate of silver, as a brown powder, which becomes of a darker colour when dried. The powder was found to be anhydrous by Gay-Lussac and Thénard; its density is 7·143, according to J. Herapath; 7·250, according to P. Boullay; 8·2558, according to Karsten. Oxide of silver is decomposed by light, or at a red heat, into oxygen gas and metallic silver. Hydrogen reduces it even at 212°. It is also reduced by an aqueous solution of phosphorous acid. When recently precipitated, it is decomposed by aqueous sulphurous acid, yielding metallic silver and sulphate of silver; but the decomposition is only partial, even when aided by heat. When immersed in water, it is reduced by zinc, cadmium, tin, and copper, but not by iron or mercury. In an aqueous solution of hypochlorous acid, it is converted into chloride of silver, oxygen being evolved together with a small quantity of chlorine.

Oxide of silver is a powerful base, and forms salts, several of which have been found isomorphous with the corresponding salts of soda. Like oxide of lead, it dissolves to a small extent in pure water free from saline matter, and the solution has an alkaline reaction. Oxide of silver is not dissolved by solutions of the hydrates of potash and soda. Its salts are precipitated black by *hydrosulphuric* acid and *alkaline sulphides*. When treated with *hydrochloric* acid or a *soluble chloride*, they yield a white curdy precipitate, the chloride of silver, which soon becomes purple, if exposed, while moist, to the direct rays of the sun. This precipitate is not dissolved by nitric acid, but is dissolved by ammonia in common with most of the insoluble salts of silver. This precipitate is visible, according to Lassaigne, even in solutions containing only 1 part of silver in 800,000 parts of liquid. In a solution containing 1 part of silver in 200,000 parts, hydrochloric acid or common salt produces a slight turbidity: with 1 part of silver in 400,000, the same reagents produce a scarcely perceptible opalescence; and if the proportion of liquid amounts to 800,000 parts, the opalescence does not show itself for a quarter of an hour. *Hydrobromic acid* and soluble metallic *bromides*, added to solutions of silver salts, throw down all the silver in the form of yellowish white bromide, insoluble in nitric acid, and sparingly soluble in ammonia. *Hydriodic* acid and soluble *iodides* form a pale yellow precipitate of iodide of silver, likewise insoluble in nitric acid, and still less soluble in ammonia. *Hydrocyanic* acid and soluble *cyanides* throw down a white precipitate of cyanide of silver, easily soluble in ammonia, insoluble in cold dilute nitric acid, but dissolved by strong nitric acid at a boiling heat, with evolution of nitric oxide. *Ammonia* added in very small quantity to perfectly neutral silver-salts, produces a slight brown precipitate of oxide of silver, easily soluble in excess; but if the solution contains excess of acid, ammonia produces no precipitate. *Potash* added to the ammoniacal solution pro-

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* Ann. Ch. Pharm. xxx. 1.

† Ann. Ch. Phys. [2], ix. 107.

duces a white precipitate, provided the excess of ammonia be but small. The *fixed alkalies* form, in neutral or acid solutions of silver-salts, a brown precipitate of oxide of silver, insoluble in excess. *Alkaline carbonates* precipitate white carbonate of silver, soluble in ammonia and carbonate of ammonia. *Ordinary tribasic phosphate of soda* forms a yellow precipitate; *pyrophosphate* and *metaphosphate of soda* form white precipitates. *Chromate of potash* forms a dark crimson precipitate of chromate of silver. *Alkaline arsenites* form a canary-yellow precipitate of arsenite of silver. *Oxalic acid* forms a white pulverulent precipitate of oxalate of silver. Silver is precipitated from its solutions in the metallic state by *phosphorus, phosphorous acid, phosphuretted hydrogen,* and *sulphurous acid* (imperfectly); by various *metals,* viz., zinc, cadmium, tin, lead, iron, manganese, copper, mercury, bismuth, tellurium, antimony, and arsenic; also by protoxide of uranium, hydrated protoxide of manganese, and protoxide of tin; and by various *organic substances* at a boiling heat, *e. g.,* charcoal, sugar, aldehyde, formic acid, tincture or infusion of galls, and volatile oils. Many organic substances added to a solution of nitrate of silver mixed with excess of ammonia, throw down metallic silver in the form of a beautiful specular film, lining the sides of the vessel. This effect is produced by aldehyde, saccharic acid, salicylous acid, pyromeconic acid, and various essential oils. A mixture of oil of cinnamon and oil of cloves is found to produce an exceedingly brilliant speculum, and has indeed been used for silvering mirrors in place of the ordinary process with tin and mercury; it is particularly adapted for silvering curved surfaces. A very bright and regular specular surface is also produced by adding a solution of milk-sugar to an ammoniacal solution of nitrate of silver mixed with caustic potash or soda; the precipitation then takes place without the application of heat (Liebig).*

Oxide of silver combines with ammonia and forms the fulminating *ammoniuret of silver,* a substance of a dangerous character from the violence with which it explodes. The ammoniuret may be formed by digesting newly precipitated oxide of silver in strong ammonia, or more readily by dissolving nitrate of silver in ammonia, and precipitating the liquor by potash in slight excess. If this substance be pressed by a hard body, while still moist, it explodes with unequalled violence; when dry, the touch of a feather is often sufficient to cause it to fulminate. The explosion is obviously occasioned by the reduction of the silver from the combination of its oxygen with the hydrogen of the ammonia, and the evolution of nitrogen gas.

Sulphide of silver, AgS, 124 *or* 1550. — Sulphur and silver may be combined together by fusion; the excess of sulphur escapes, and at a high temperature the sulphide melts; it forms, on cooling, a crystalline mass. This compound has a lead-grey colour and metallic lustre. It is so soft that it may be cut with a knife, and is malleable. The sulphide of silver is also remarkable for conducting electricity, like a metal, when warmed. The same compound occurs in nature, sometimes crystallized in octohedrons with secondary faces. This sulphide is particularly interesting from being isomorphous with the sulphide of copper, AgS with Cu_2S (p. 501). These two sulphides replace each other in indeterminate proportions in several double sulphides of silver and other metals, as in *polybasite* and *fahl-ores,* the composition of which may be expressed by the following formulæ, the symbols placed above each other representing constituents, of which either the one or the other may be present:

$$\text{Polybasite} \quad . \quad 9\genfrac{}{}{0pt}{}{Cu_2S}{AgS} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}$$

$$\text{Fahl-ores} \quad \left(4\genfrac{}{}{0pt}{}{ZnS}{FeS} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}\right) + 2\left(4\genfrac{}{}{0pt}{}{AgS}{Cu_2S} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}\right).$$

Chloride of silver, $AgCl$, 143·5 *or* 1793·75. — This salt contains, in 100 parts,

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* Ann. Ph. Pharm. xcviii. 132.

24·69 parts of chlorine, and 75·31 parts of silver. It is found native as *horn-silver,* in translucent cubes or octohedrons of a greyish-white colour, and specific gravity 5·55. The same compound is also thrown down as a white precipitate, at first very bulky and curdy, when hydrochloric acid or a soluble chloride is added to any soluble salt of silver, except the hyposulphite. It is wholly insoluble in water, and the most minute quantity of hydrochloric acid contained in water may be detected by adding to it a drop of a solution of nitrate of silver. Hydrochloric acid, when concentrated, dissolves chloride of silver, which crystallizes from it in octohedrons, when the solution is evaporated. This salt dissolves easily in solution of ammonia, and crystallizes also as the ammonia evaporates. When heated, it fuses at about 500°, forming a transparent yellowish liquid, which becomes, after cooling, a mass that may be cut with a knife, and has considerable resemblance to horn: a property to which it was indebted for the name of *horn-silver,* applied to it by the older chemists. It is not volatile. Chloride of silver is not affected by a concentrated solution of potash. It is easily reduced to the state of metal by zinc or iron with water. Chloride of silver may be dissolved out in this way by means of zinc and acidulated water, from a porcelain crucible in which it has been fused. To obtain pure silver by this mode of reduction, it is necessary to use zinc free from lead, otherwise that metal, not being dissolved by the sulphuric acid, remains mixed with the silver. A better mode of reduction is to boil the chloride of silver with an equal weight of starch-sugar and a solution of one part of carbonate of soda in three parts of water (Böttger). The chloride and other salts of silver acquire a dark colour when exposed to light; chlorine escapes, and a portion of the salt appears to be reduced to the metallic state, as the blackened surface conducts electricity. According to Wetzlar, the black substance contains an inferior chloride of silver, and is not attacked by nitric acid, or soluble in ammonia. It has also been supposed that the blackening is due, not to any chemical decomposition, but merely to a change in the state of aggregation of the particles. It appears, however, from some recent experiments by Dr. F. Guthrie, that the chloride is completely decomposed and metallic silver separated, even in presence of free nitric acid. Paper charged with chloride of silver is very sensitive to the impression of light, and is the material used for positive photographs, the unaltered chloride being afterwards dissolved out by a solution of hyposulphite of soda.

One hundred parts of chloride of silver absorb 17·9 parts of ammoniacal gas, forming the compound, $3NH_3.2AgCl$, or $\left.\begin{array}{r}\mathrm{N}\overbrace{\mathrm{H(NH_4)_2Ag}}\\ \mathrm{Ag}\end{array}\right\}\mathrm{Cl_2}$. This compound gives off its ammonia in the air. Chloride of silver is dissolved by concentrated and boiling solutions of the chlorides of potassium, sodium, and ammonium, and, on cooling, a double salt is deposited in crystals, generally cubes. Chloride of silver is also dissolved by cyanide of potassium, and the solution yields a double salt by evaporation (Liebig).

Bromide of silver, AgBr, 188 *or* 2350.—This salt consists in 100 parts, of 42·56 bromine and 57·44 silver. It is found native in Mexico and in Bretagne; sometimes in small amorphous masses, sometimes in greenish-yellow octohedral crystals. It is insoluble in water, and falls as a precipitate which is white at first, but becomes pale yellow when collected. When fused and cooled, it yields a mass of a pure and intense yellow colour. It has most of the properties of chloride of silver, but dissolves very sparingly in ammonia.

Iodide of silver, AgI, 234·36 *or* 2929·5.—This salt contains, in 100 parts, 53·87 of iodine and 46·13 of silver. It is found native, sometimes in regular hexagonal prisms. It is insoluble in water, like the chloride, and is prepared in a similar manner by precipitation, but is distinguished from that salt by its colour, which is pale yellow, by the difficulty with which it is dissolved in ammonia, being even less soluble than the bromide, and by being blackened more slowly by the action of light. According to Martini, 2500 parts of ammonia, of density 0·960, are required to dissolve one part of iodide of silver. It is soluble to a large extent, at the boiling temperature, in concentrated solutions of the alkaline and earthy iodides, and forms with them double salts.

Silver is rapidly dissolved by hydriodic acid, with evolution of hydrogen. If the action is assisted by heat, the solution deposits, on cooling, a colourless crystalline salt, resembling nitrate of silver, but decomposing as soon as it is separated from the liquid: it appears to consist of an iodide of silver and hydrogen. The mother-liquor, when left to itself, deposits iodide of silver in large regular six-sided prisms, resembling the native iodide (H. Ste.-Claire Deville).*

Fluoride of silver, AgF, is obtained by dissolving the oxide or carbonate in hydrofluoric acid. It is very soluble in water, and is partly decomposed by evaporation.

Cyanide of silver, AgCy; 134 *or* 1675.—This salt contains, in 100 parts, 19·41 cyanogen and 80·59 silver. It falls as a white powder when hydrocyanic acid is added to a solution of nitrate of silver. It is distinguished from chloride of silver by dissolving in concentrated nitric and sulphuric acids, when heated. It is readily decomposed by hydrochloric acid, and yields hydrocyanic acid, 100 parts of cyanide of silver giving 20·36 parts of hydrocyanic acid. It is decomposed by a red heat, giving off half its cyanogen and leaving paracyanide of silver, Ag_6Cy_3. Cyanide of silver is dissolved by cyanide of potassium, and other soluble cyanides. The double cyanide of potassium and silver crystallizes in octohedrons, KCy.AgCy.

Carbonate of silver, $AgO.CO_2$, is a white insoluble powder.

Sulphate of silver, $AgO.SO_3$; 156 *or* 1950.—Obtained by dissolving silver, with heat, in concentrated sulphuric acid, or by precipitating a solution of nitrate of silver with sulphate of potash. It is soluble in 88 times its weight of boiling water, and crystallizes, on cooling, in the form of anhydrous sulphate of soda. This salt is highly soluble in ammonia, and gives, by evaporation, an ammoniacal sulphate of silver in fine transparent crystals, which are persistent in air; $AgO.SO_3 + 2NH_3$, or $\overparen{NH_2(NH_4)Ag}.SO_4$. Chromate and seleniate of silver form analogous compounds with ammonia, which are all isomorphous. The bichromate of silver is also isomorphous with bichromate of soda.

Hyposulphate of silver, $AgO.S_2O_5$, is soluble in water, and crystallizes in the same form as hyposulphate of soda. It crystallizes also with ammonia, as $AgO.S_2O_5 + 2NH_3$, or $\overparen{NH_2(NH_4)Ag}.S_2O_6$.

Hyposulphite of silver, $AgO.S_2O_2$.—Hyposulphurous acid appears to have a greater affinity for oxide of silver than for any other base. Oxide of silver decomposes the alkaline hyposulphites, liberating one half of their alkali, and forming a double hyposulphite of the alkali and silver. These double salts are best prepared by adding chloride of silver in small portions to the soluble hyposulphite of potash, soda, ammonia, or lime in the cold, till the liquid is saturated; after which, the solution is filtered, and mixed with a large quantity of alcohol, which precipitates the double salt; the potash and soda salts are crystallizable. Herschel considers the double salts obtained in this manner as probably containing one eq. of hyposulphite of silver to two eq. of the other hyposulphite. The solution of one of these double salts dissolves more oxide of silver, and forms a double salt, which is believed to contain single equivalents of the salts, and precipitates as a white crystalline, pulverulent, bulky mass. The second compound is sparingly soluble in water, but dissolves in ammonia, and communicates to the liquor an intensely sweet taste.

The hyposulphite of silver itself is an insoluble substance; it is prone to undergo decomposition, changing spontaneously into sulphate and sulphide of silver.

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* Compt. rend. xlii. 894.

When to a dilute solution of nitrate of silver, a dilute solution of hyposulphite of soda is added by small quantities, a white precipitate of hyposulphite of silver falls, which dissolves again in a few seconds, from the formation of the soluble double hyposulphite of soda and silver. When enough of hyposulphite of soda has been gradually added to render the precipitate permanent, without, however, decomposing the whole silver salt, a flocculent mass is obtained of a dull grey colour, which is permanent. The liquor contains much hyposulphite of silver, and has an intensely sweet taste, not at all metallic; the silver is not precipitated from it by hydrochloric acid or the chlorides. An excess of hyphosulphate of soda destroys the precipitated hyposulphite of silver, converting it into sulphide of silver.

Nitrate of silver, $AgO.NO_5$; 170 *or* 2125. — When a piece of pure silver is suspended in nitric acid, it dissolves for a time without effervescence at a low temperature, nitrous acid being produced, which colours the liquid blue; but if heat be applied or the temperature allowed to rise, then the metal dissolves with violent effervescence, from the escape of nitric oxide. The nitrate of silver crystallizes on cooling in colourless tables, which are anhydrous. It is soluble in 1 part of cold, in ½ part of hot water, and in 4 parts of boiling alcohol. The solution of this salt does not redden litmus paper, like most metallic salts, but is exactly neutral. Nitrate of silver fuses at 426°, and forms a crystalline mass on cooling; it is cast into little cylinders for the use of surgeons. It is sometimes adulterated in this state with nitrate of potash, which may be detected by the alkaline residue which the salt then leaves when heated before the blowpipe, — or with nitrate of lead, in which case the solution of the salt is precipitated by iodide of potassium, of a full yellow colour. When applied to the flesh of animals, it instantly destroys the organization and vitality of the part. It forms insoluble compounds with many kinds of animal matter, and is employed to remove it from solution. When organic substances, to which a solution of nitrate of silver has been applied, are exposed to light, they become black from the reduction of the oxide of silver to the metallic state. A solution of nitrate of silver in ether is employed to dye the hair black. One part of nitrate of silver and 4 parts of gum arabic dissolved in 4 parts of water, and blackened with a small quantity of Indian ink, form the indelible marking ink used to write upon linen. The part of the linen to be marked should be first wetted with a solution of carbonate of soda and dried, and the writing should be exposed to the light of the sun. For this ink, which is expensive, another liquid has been substituted by bleachers, namely coal tar, made sufficiently thin with naphtha to write with, which is found to resist chlorine, and to answer well as a marking ink.

A strong solution of nitrate of silver absorbs two equivalents of ammoniacal gas, and forms the crystallizable *Ammoniacal nitrate of silver*, $Ago.NO_5 + 2NH_3 = \overbrace{NH_2(NH_4)Ag.N}O_6$. The dry nitrate in powder absorbs three atoms of ammonia, $AgO.NO_5 + 3NH_3 = \overbrace{NH(NH_4)_2Ag.N}O_6$.

Nitrate of silver forms a double salt with nitrate of the red oxide of mercury, which crystallizes in prisms. Nitrate of silver and cyanide of mercury also form a double salt, when hot solutions of them are mixed: $AgO.NO_5 + 2HgCy + 8HO$. Cyanide of silver is soluble in a boiling solution of nitrate of silver, and forms a crystalline compound, $Ago.NO_5 + 2AgCy$, which is decomposed by water.

Nitrite of silver, $AgO.NO_3$; 154 or 1925. — Nitrate of soda is fused at a red heat, till it is wholly converted into nitrite by loss of oxygen; the latter salt then begins to give off nitrous acid, and a small portion of the salt dissolved in water will be found to precipitate silver brown. The fusion is then interrupted, the salt dissolved in boiling water, precipitated by nitrate of silver, and filtered while still very hot. The nitrite of silver, which requires 120 times its weight of water at 60° to dissolve it, is precipitated as the solution cools. The other nitrites are prepared by rubbing this salt in a mortar with chlorides taken in equivalent quantities. It appears from experiments of Proust, that two subnitrites of silver exist, one soluble and the other insoluble.

Acetate of silver, which is soluble in 100 times its weight of cold water, is precipitated when acetate of copper is mixed with a concentrated solution of nitrate of silver It crystallizes from solution in boiling water in anhydrous needles.

Oxalate of silver is an insoluble powder. A double *oxalate of potash and silver* is formed by saturating binoxalate of potash with carbonate of silver. It is very soluble, and forms rhomboidal crystals, which are persistent in air.

Peroxide of silver. — A superior oxide of silver is deposited upon the positive pole or zincoid of a voltaic battery in a weak solution of nitrate of silver, in the form of needles of 3 or 4 lines in length, which are black and have a metallic lustre, while metallic silver is, at the same time, deposited in crystals upon the negative pole or chloroid. The former crystals are converted by sulphuric acid into oxide of silver and oxygen, and yield with hydrochloric acid, chloride of silver and chlorine. According to Fischer, whose observations are confirmed by L. Gmelin, the peroxide prepared as above from nitrate of silver always retains nitric acid, and if prepared in a similar manner from the sulphate, it always retains sulphuric acid.*

Alloys of silver.—Silver may be readily alloyed with most metals. It combines by fusion with iron, from which it cannot be separated by cupellation. Native silver is always associated with gold; the two metals are found crystallized together in all proportions in the same cubic or octohedral crystals. Gold may be detected in a silver coin, by dissolving the latter in pure nitric acid, when a small quantity of black powder remains, which after being washed with water, will be found to dissolve in nitro-hydrochloric acid, giving a yellow solution, in which protochloride of tin produces a precipitate of the purple powder of Cassius. Pure silver, being very soft, is always alloyed in coin and plate, with a certain quantity of copper, to make it harder. The standard silver of England is an alloy of 222 pennyweights of silver with 18 pennyweights of copper, or it contains 92·5 per cent. of silver. The standard of the Spanish dollar, of the French and most other coinages, is 90 per cent. of silver. The alloy of silver and copper of greatest stability consists of 71·9 silver, and 28·1 copper, and corresponds with the formula $AgCu_4$.†

ESTIMATION OF SILVER, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Silver, when in the state of solution, is always estimated as chloride. The solution, if not already acid, is slightly acidulated with nitric acid; the silver precipitated with hydrochloric acid, and the liquid placed for some hours in a warm situation to cause the precipitated chloride of silver to settle down. The precipitate is collected on a filter, which should be as small as possible, washed with water, and dried at 212°. It must then be separated as completely as possible from the filter; introduced into a porcelain crucible, previously weighed; the filter burnt to ashes outside the crucible; the ashes added to the contents of the crucible; and the whole strongly heated over a lamp till the chloride of silver is brought to a state of tranquil fusion, after which it is left to cool and weighed. It contains 75·26 per cent. of silver. This mode of estimation is affected with an error, arising from the partial reduction of the chloride of silver by the organic matter of the filter. The error thus occasioned is but slight when the process is well conducted, and may always be obviated by treating the fused chloride after cooling with nitric acid to dissolve the reduced silver; then adding hydrochloric

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* Gmelin's Handbook, Translation, vi. 145.

† Levol, Ann. Ch. Phys. [3], xxxvi. 220.

acid, evaporating to dryness, and again fusing the residue. Another mode of proceeding is to collect the chloride of silver on a weighed filter, and dry it in an oil-bath at about 300° F. The chloride may also be washed by decantation, and the use of a filter avoided altogether; but the washing requires very careful manipulation.

The quantity of silver in a solution may also be determined by precipitating it with a solution of chloride of sodium of known strength. The solution of chloride of sodium is made of such a strength that a cubic decimetre of it exactly precipitates 1 gramme of pure silver. It is added to the silver solution from a burette, divided into cubic centimetres, the liquid being well shaken after each addition, to cause the precipitate to settle down. The number of cubic centimetres of solution thus added determines the quantity of silver present.

As silver is reduced from many of its salts by the mere action of heat, the quantity of silver in such compounds may be readily determined by simply igniting them in a porcelain crucible. This method is applicable to nearly all salts of silver which contain organic acids. It must be observed, however, that in some cases, a certain quantity of carbon remains combined with the silver, and that some organic silver compounds containing nitrogen leave cyanide of silver when ignited.

The method of precipitating by hydrochloric acid serves to separate silver from all other metals. If lead be present in solution with silver, the liquid must be diluted with a large quantity of water before the hydrochloric acid is added; because the chloride of lead is but sparingly soluble. The separation of silver from lead may also be effected by precipitating both the metals as chlorides, and dissolving the chloride of silver in ammonia. To separate silver from mercury, the latter metal, if in the state of mercurous oxide, must first be converted into mercuric oxide by oxidation with nitric acid.

The estimation of the quantity of silver in alloys, such as coins, is usually effected either by cupellation in the manner already described (p. 593), or by dissolving the alloy in nitric acid, and precipitating the silver with a graduated solution of chloride of sodium.*

The cupellation of silver is always attended with a certain loss, arising partly from a portion of the melted silver being absorbed by the cupel, and partly by volatilization. The loss thus occasioned varies with the proportion of lead employed in the cupellation, with the proportion of silver in the alloy, and likewise with the heat of the furnace: hence the results obtained require a certain correction, the amount of which must be determined by special trials made upon alloys of known composition and with different proportions of lead.

SECTION III.

GOLD.

Eq. 98·33 *or* 1229·16; Au. (*Aurum*).

Gold is found in small quantity in most countries, sometimes mixed with iron pyrites, copper pyrites, and galena, but generally native, massive, and disseminated in threads through crystalline rocks, such as quartz, or in grains among the sand of rivers, and in alluvial deposits formed by the disintegration of ancient rocks. In these deposits, some of which are of great extent, gold is occasionally found in masses of considerable size, called *nuggets*. Formerly, the principal sup-

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* The process, by Gay-Lussac, for this purpose is described, with the requisite Tables, in the Parliamentary Report upon the Royal Mint, 1837, Appendix, p. 145. See also *Dr. Miller's Elements of Chemistry*, p. 1035.

ply of this metal was from the mines of South America, Hungary, and the Uralian mountains; but of late years, the largest quantities have been obtained from California and Australia. Native gold is sometimes pure, but is more frequently associated in various proportions with silver.

Gold is separated from the substances with which it is mechanically associated, either by washing with water, whereby the earthy matters are carried away while the heavy gold particles remain behind, or by amalgamation. The small quantity of gold which occurs, generally associated with silver, in certain lead and copper ores, is extracted by liquation and cupellation, in the manner already described for silver. By these processes, gold is obtained free from all other metals except silver, and from this it may be separated by nitric acid, which dissolves the silver, but only when it forms a large proportion of the alloy. When nitric acid does not dissolve the silver, the alloy is submitted to an operation termed *quartation*, which consists in fusing it with four times its weight of silver, after which the whole of the silver may be dissolved out by nitric acid.

Pure gold may be obtained from any alloy containing it, by dissolving the alloy in a mixture of two measures of hydrochloric and one measure of nitric acid; separating the solution from insoluble chloride of silver by filtration; evaporating it over the water-bath till acid vapours cease to be exhaled; then dissolving the residue in water acidulated with hydrochloric acid; and adding protosulphate of iron, which completely precipitates the gold in the form of a brown or brownish-yellow powder, the protosulphate of iron being at the same time converted into sesquisulphate and sesquichloride:

$$6(FeO\,.\,SO_3) + Au_2Cl_3 = 2(Fe_2O_3\,.\,3SO_3) + Fe_2Cl_3 + 2Au.$$

The gold thus precipitated is quite destitute of metallic lustre, but acquires that character by burnishing.

From alloys of gold and silver, or of gold, silver, and copper, the gold may also be separated by the action of strong sulphuric acid. The alloy, after being granulated by pouring it in the melted state into water, is heated in a platinum or cast-iron vessel with 2½ times its weight of sulphuric acid of specific gravity 1·815 (66° Baumé), the heat being continued as long as sulphurous acid is evolved. The silver and copper are thereby converted into sulphates, while the gold remains unattacked. The solution is boiled for a quarter of an hour with an additional quantity of sulphuric acid of specific gravity 1·653, or 58° Baumé (obtained by concentrating the acid mother-liquors of sulphate of copper produced in the operation), and afterwards left at rest. The gold then settles down, and the liquid, after being diluted with water, is transferred to a leaden vessel and again boiled with sheets of copper immersed in it. The silver is then precipitated in the metallic state, while the copper is converted into sulphate, and dissolves. The gold deposited in the manner above described still retains a small quantity of silver, from which it is separated by treating it a second and a third time with strong sulphuric acid: it then retains only 0·005 of silver. This process is not applicable to alloys containing more than 20 per cent. of gold; richer alloys must first be fused with the requisite quantity of silver. It is applied on the large scale to the extraction of gold, chiefly from alloys which contain but little of that metal, such as native silver and old silver coins, and, as now practised, is economically available even when the amount of gold does not exceed one part in 2000.

Gold is the only metal of a yellow colour. When pure, it is more malleable than any other metal, and nearly as soft as lead. Its ductility appears to have scarcely a limit. A single grain of gold has been drawn into a wire 500 feet in length, and this metal is beaten out into leaves which have not more than 1-200,000 of an inch of thickness. The coating of gold on gilt silver wire is still thinner. Gold, when very thin, is transparent, thin gold leaf appearing green by transmitted light. The green colour passes into a ruby red when highly attenuated gold is heated: in the red gold-glass, the gold is in the metallic state (Faraday).

The point of fusion of this metal is 2192°, according to Pouillet; 2518°, according to Guyton-Morveau; 2590°, according to Daniell: it contracts considerably upon becoming solid. The density of gold varies from 19·258 to 19·367, according as it has been more or less compressed. Gold does not oxidate or tarnish in air, at the usual temperature, nor when strongly ignited. But this and the other noble metals are dissipated and partly oxidated, when a powerful electric charge is sent through them in thin leaves. It is not dissolved by nitric, hydrochloric, or sulphuric acid, or indeed by any single acid. It is acted upon by chlorine, which converts it into sesquichloride, and by acid-mixtures, such as aqua-regia, which evolve chlorine. It combines in two proportions with oxygen, forming the two oxides Au_2O and Au_2O_3, which show but little tendency to combine with acids. Some chemists, however, double the atomic weight of gold, and regard these oxides as protoxide, AuO, and teroxide, AuO_3, respectively.

Oxide of gold, Aurous oxide, Au_2O, 204·66 *or* 2558·25.—This oxide is obtained as a green powder by decomposing the corresponding chloride of gold with a cold solution of potash. It is partly dissolved by the alkali, and soon begins to undergo decomposition, being resolved into the higher oxide and metallic gold. The latter forms upon the sides of the vessel a thin film, which is green by transmitted light, like gold leaf.

Chloride of gold, Aurous chloride, Au_2Cl, is obtained by evaporating a solution of the sesquichloride to dryness, and heating the powder thus obtained in a sand-bath, retaining it at about the temperature of melting tin, and constantly stirring it, so long as chlorine is evolved. It is a white, saline mass, having a tinge of yellow, and quite insoluble in water. In the dry state it is permanent, but in contact with water it gradually undergoes decomposition, and is converted into gold and the sesquichloride. This change takes place almost instantaneously at the boiling temperature.

Aurous iodide, Au_2I, is formed by the action of hydriodic acid on auric oxide, water being formed and two-thirds of the iodine set free:

$$Au_2O_3 + 3HI = Au_2I + 3HO + 2I;$$

also by adding iodide of potassium in proper proportion, and in successive small quantities, to an aqueous solution of auric chloride:

$$Au_2Cl_3 + 3KI = Au_2I + 3KCl + 2I.$$

It is a lemon-yellow, crystalline powder, insoluble in cold water, and very sparingly soluble in boiling water.

Aurous sulphide is formed when hydrosulphuric acid gas is passed into a boiling solution of the sesquichloride of gold. It is dark-brown, almost black. Aurous sulphide combines with the protosulphides of potassium and sodium, forming double salts containing 1 eq. of aurous sulphide with 1 eq. of the alkaline sulphide. The sodium-salt is obtained by fusing together 2 eq. protosulphide of sodium, 1 eq. gold, and 6 eq. sulphur; digesting the fused mass in water; filtering the yellow solution in an atmosphere of nitrogen; and concentrating in vacuo over sulphuric acid. Yellow crystals are then obtained, having the form of oblique hexagonal prisms with trilateral or quadrilateral summits, and containing $NaS.Au^2S + 8Aq$. They are soluble in water and alcohol. The potassium-salt, which is obtained in a similar manner, forms indistinct crystals (Col. Yorke).*

Sesquioxide of gold, Auric oxide, Au_2O_3, 220·66 *or* 2758·25.—This oxide has many of the properties of an acid. It is obtained by digesting magnesia in a solution of sesquichloride of gold, when an insoluble compound of auric oxide and magnesia is formed, which is collected upon a filter and well washed. The compound is afterwards digested in nitric acid, which dissolves the magnesia, with traces of auric oxide, but leaves the greater part of the latter undissolved. It is

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* Chem. Soc. Qu. J. i. 236.

left in the state of a reddish-yellow hydrate, which when dried in air becomes chestnut-brown. When precipitated by an alkali, auric oxide carries down a portion of the latter, of which it may be deprived by nitric acid. Dried at 212°, it abandons its water, becomes black, and is in part reduced. When exposed to light, particularly to the direct rays of the sun, its reduction is very rapid. It is decomposed by an incipient red heat. Hydrochloric acid is the only acid which dissolves and retains this oxide, and then sesquichloride of gold is formed. It is dissolved by concentrated nitric and sulphuric acid, but precipitated from these solutions by water. The affinity of this oxide for alkaline oxides, on the contrary, is so great that, when boiled in a solution of chloride of potassium, it is dissolved, the liquid becoming alkaline, and *aurate of potash*, or a compound of auric oxide and potash, being formed. The compounds of auric oxide with the alkalies and alkaline oxides are nearly colourless, and are not decomposed by water. They appear to be of two different degrees of saturation, aurates which are soluble, and superaurates which are insoluble. The only one of these compounds which has been studied in some degree is the aurate of ammonia, or *fulminating gold* as it is named, from its violently explosive character.

Aurate of ammonia. — When the solution of gold is precipitated by a small quantity of ammonia, a powder of a deep yellow colour is obtained, which is a compound of aurate of ammonia with a portion of sesquichloride of gold. This compound explodes by heat, but the detonation is not strong. But when the solution of gold is treated with an excess of ammonia, and the precipitate well washed by ebullition in a solution of ammonia, or better in water containing potash, the fulminating gold has a yellowish brown colour with a tinge of purple. When dry, it explodes very easily with a loud report, accompanied by a feeble flame. It may be exploded by a heat a little above the boiling point of water, or by the blow of a hammer. Its composition has not been exactly determined; but if the ammonia is present in double the proportion that would contain the hydrogen necessary to burn the oxygen of the auric oxide, which Berzelius considers probable, its constituents may be $Au_2O_3.2NH_3 + HO$. The affinity of auric oxide for ammonia is so great, that it takes that alkali from all acids. Thus, when auric oxide is digested in sulphate of ammonia, fulminating gold is formed, and the liquid becomes acid.

Aurate of potash, $KO.Au_2O_3 + 6HO$. — Obtained in the crystalline state by evaporating a solution of sesquioxide of gold in a slight excess of pure potash, first over the open fire and afterwards in vacuo: the crystals may be freed from adhering potash by recrystallization from water, then drained on unglazed porcelain and dried in vacuo. Aurate of potash is very soluble in water, and forms a yellowish strongly alkaline solution, which is decomposed by nearly all organic bodies, the gold being precipitated in the metallic state: it is also decomposed by heat. With most metallic salts it forms precipitates of aurates, which are insoluble in water, but soluble in excess of the precipitant; thus, chloride of calcium forms a precipitate of aurate of lime, soluble in excess of chloride of calcium. The solution of aurate of potash may be used as a bath for electro-gilding.

Aurosulphite of potash, $KO.Au_2O_3 + 4(KO.2SO_2) + 5HO$; or $5KO\left\{\begin{matrix}Au_2O_3\\8SO_2\end{matrix}\right. + 5HO$.—Deposited in beautiful yellow needles when sulphite of potash is added drop by drop to an alkaline solution of aurate of potash. It is nearly insoluble in alkaline solutions, but dissolves with decomposition in pure water, especially if hot, giving off sulphurous acid and depositing metallic gold. Acids decompose it in a similar manner. After drying in vacuo, it may be preserved for two or three months, in well-closed bottles, but ultimately decomposes, giving off sulphurous acid and leaving metallic gold and sulphate of potash. The same decomposition takes place more quickly when the salt is heated (Fremy).*

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* Ann. Ch. Pharm. lvi. 315.

Purple of Cassius. — When protochloride of tin is added to a dilute solution of gold, a purple-coloured powder falls, which has received that name. It is obtained of a finer tint when protochloride of tin is added to a solution of the sesquichloride of iron, till the colour of the liquid takes a shade of green, and the liquid in that state added, drop by drop, to a solution of sesquichloride of gold free from nitric acid, and very dilute. After 24 hours, a brown powder is deposited, which is slightly transparent, and purple-red by transmitted light. When dried and rubbed to powder, it is of a dull blue colour. Heated to redness, it loses a little water, but no oxygen, and retains its former appearance. If washed with ammonia on the filter while still moist, it is dissolved, and a purple liquid passes through, which rivals the hypermanganate of potash in beauty. From this liquid, the colouring matter separates very gradually, weeks elapsing before the upper strata of the liquid become colourless; but it is precipitated more rapidly when heated in a close vessel between 140° and 180°. The powder of Cassius is insoluble in solutions of potash and soda. It may also be formed by fusing together 2 parts of gold, 3½ parts of tin, and 15 parts of silver, under borax, to prevent the oxidation of the tin, and treating the alloy with nitric acid to dissolve out the silver; a purple residue is left containing the tin and gold that were employed.

The powder of Cassius is certainly, after ignition, a mixture of binoxide of tin and metallic gold, from which the gold can be dissolved out by aqua-regia, while the binoxide of tin is left; and the last mode of preparing it, favours the idea that its constitution is the same before ignition; but the solubility of the unignited powder in ammonia, and the fact that mercury does not dissolve out gold from the powder when properly prepared, appear to be conclusive against that opinion. The proportions of its constituents vary so much, that there must be more than one compound; or more likely the colouring compound combines with more than one proportion of binoxide of tin. Berzelius proposed the theory that the powder of Cassius may contain the true protoxide of gold combined with sesquioxide of tin, $AuO.Sn_2O_3$, a kind of combination containing an association of three atoms of metal, which is exemplified in black oxide of iron, spinell, gahnite, franklinite, and other minerals, and which we have repeatedly observed to be usually attended with great stability. A glance at its formula shows how readily the powder of Cassius, as thus represented, may pass into gold and binoxide of tin; $AuO.Sn_2O_3 = Au + 2SnO_2$. The existence of a purple oxide of gold, AuO, is not established; but it is probably the substance formed when a solution of gold is applied to the skin or nails, and which dyes them purple. Paper, coloured purple by a solution of gold, becomes gilt when placed in the moist state in phosphuretted hydrogen gas, which reduces the gold to the metallic state.

Pelletier gives the following method of preparing a purple of Cassius of constant composition: — 20 grammes of gold are dissolved in 100 grammes of aqua-regia containing 20 parts nitric to 80 parts of commercial hydrochloric acid; the solution is evaporated to dryness over the water-bath; the residue dissolved in water; the filtered solution diluted with 7 or 8 decilitres of water; and tin filings introduced into it: in a few minutes the liquid becomes brown and turbid, and deposits a purple precipitate, which merely requires to be washed and dried at a gentle heat. The purple thus prepared contains in 100 parts: 32·746 stannic acid, 14·618 protoxide of tin, 44·772 aurous oxide (Au_2O) and 7·864 water. The precipitate obtained by treating sesquichloride of gold with pure protochloride of tin is always brown. To obtain a fine purple precipitate, the chloride of gold should be treated with a mixture of protochloride and bichloride of tin. The following process gives a fine purple:—*a.* A neutral solution is prepared of 1 part of tin in hydrochloric acid; *b.* A solution of 2 parts tin in cold aqua-regia (1 part hydrochloric acid to 3 nitric), the liquid being merely heated towards the end of the process, that it may not contain any protoxide of tin; *c.* Seven parts of gold are dissolved in aqua-regia (6 hydrochloric to 1 nitric), and the solution, which is nearly neutral, diluted with 3500 parts of water. To this solution *c*, the solution *b* is first added, and then the solution *a*, drop by drop, till the proper colour is produced. If the quantity of *a* be too small, the precipitate is violet; if too large, it is brown. It must be washed quickly, so that the liquid may not act upon it too long. It weighs 6½ parts (Bouisson).*

Sesquisulphide of gold, Au_2S_3, or *Auric sulphide*, is formed when a dilute solution of gold is precipitated cold by hydrosulphuric acid. It is a flocculent matter of a strong yellow colour, which becomes deeper by drying; it loses its sulphur at a moderate heat.

Sesquichloride of gold, Perchloride of gold, Auric chloride, Au_2Cl_3, 303·16 or 3789·5.—This compound is formed when gold is dissolved in aqua-regia. The solution is yellow, and becomes paler with an excess of acid, but is of a deep red when neutral in composition. It is obtained in the last condition by evaporating the solution of gold, till the liquid is of a dark ruby colour, and begins to emit chlorine. It forms on cooling a dark red crystalline mass, which deliquesces quickly in air. But the only method of procuring auric chloride perfectly free from acid salt, is to decompose aurous chloride with water. A compound of chloride of gold and hydrochloric acid crystallizes easily from an acid solution, in long needles of a pale yellow colour, which are permanent in dry air, but run into a liquid in damp air. The solution of this salt deposits gold on its surface, and on the side of the vessel turned to the light. The gold is also precipitated in the metallic state by phosphorus, by most metals, by ferrous salts, by arsenious and antimonious acids, and by many vegetable and animal substances, by vegetable acids, by oxalate of potash, &c., carbonic acid then escaping. Hydrosulphuric acid and sulphide of ammonium throw down black sulphide of gold, soluble in excess of the latter reagent. Ammonia and carbonate of ammonia produce a yellow precipitate of fulminating gold. Potash added in excess forms no precipitate, unless it contains organic matter, in which case a slight precipitate of aurous oxide is produced. Cyanide of potassium produces a yellow precipitate soluble in excess. Tincture of galls throws down metallic gold. Chloride of gold is soluble in ether and in some essential oils. It forms double salts with most other chlorides, which are almost all orange-coloured when crystallized; in efflorescing, they acquire a lemon-yellow colour, but in the anhydrous state they are of an intense red. They are obtained by evaporating the mixed solutions of the two salts.

Chloride of gold and potassium, $KCl.Au_2Cl_3 + 5HO$.—Crystallizes in striated prisms with right summits, or in thin hexagonal tables which are very efflorescent; becomes anhydrous at 212°. The anhydrous salt fuses readily when heated, but loses chlorine and becomes a liquid, which is black while hot, and yellow when cold. It is then a compound of aurous chloride with chloride of potassium. *Chloride of gold and ammonium* crystallizes in transparent prismatic needles, which become opaque in air; Mr. Johnston found their composition to be $NH_4Cl.Au_2Cl_3 + 2HO$. *Chloride of gold and sodium* crystallizes in long four-sided prisms, and is persistent in air. Its composition is $NaCl.Au_2Cl_3 + 4HO$. Bonsdorff has prepared similar double salts with the chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadminm, cobalt, and nickel. The salt of lime contains six, and the salt of magnesia twelve equivalents of water.

Sesquibromide of gold, Au_2Br_3, is formed by dissolving gold in a mixture of nitric and hydrobromic acids. It greatly resembles the sesquichloride, and forms also an extensive series of double salts.

Auric iodide, Au_2I_3, is formed by gradually adding a neutral solution of auric chloride to a solution of iodide of potassium: the liquid then acquires a dark-green colour, and yields a dark-green precipitate of Au_2I_3, which redissolves on agitation; but after 1 eq. of the auric chloride has been added to 4 eqs. of iodide of potassium, a further addition of the gold-solution decolourizes the liquid and

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* J. Pharm. [2], xvi. 629.

forms a permanent precipitate of auric iodide, because the iodide of gold and potassium at first produced is thereby decomposed. The successive actions are represented by the following equations:

$$(1.)\qquad 4KI + Au_2Cl_3 = 3KCl + KI \, . \, Au_2I_3;$$

$$(2.)\qquad 3(KI \, . \, Au_2I_3) + Au_2Cl_3 = 3KCl + 4Au_2I_3$$

Auric iodide is a very unstable compound; when exposed to the air at ordinary temperatures, it is gradually converted into yellow aurous iodide, and afterwards into metallic gold. It combines with hydriodic acid and with the more basic metallic iodides, forming a series of very dark-coloured salts; e. g. *iodo-aurate of potassium*, $KI \, . \, Au_2I_3$.

The oxides of gold show but little tendency to combine with oxygen-acids: the sesquioxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution.

Hyposulphite of aurous oxide and soda:

$$Au_2O \, . \, S_2O_2 + 3(NaO \, . \, S_2O_2) + 4HO; \text{ or } \left.\begin{matrix} Au_2O \\ 3NaO \end{matrix}\right\} 4S_2O_2 + 4HO.$$

This salt is prepared by mixing concentrated solutions of sesquichloride of gold and hyposulphite of soda, and precipitating with alcohol. When purified by repeated solution in water and precipitation by alcohol, it forms delicate, colourless needles. It has a sweetish taste, dissolves very easily in water, but very sparingly in alcohol. It is decomposed by heat and by nitric acid, with deposition of metallic gold. Its solution gives a blackish precipitate with hydrosulphuric acid and soluble sulphides. The presence of gold in this solution is not indicated by protosulphate of iron, protochloride of tin, or oxalic acid; and, on the other hand, sulphuric acid, hydrochloric acid, and the vegetable acids neither precipitate sulphur nor expel sulphurous acid from it. When mixed with chloride of barium, it yields a gelatinous precipitate of *Hyposulphite of aurous oxide and baryta*, containing $\left.\begin{matrix} Au_2O \\ 3BaO \end{matrix}\right\} 4S_2O_2$. Sulphuric acid removes all the baryta from this salt, and leaves *hydrated aurous hyposulphite*, which is uncrystallizable, strongly acid, and tolerably stable at ordinary temperatures. The solution of the soda-salt is used for fixing daguerreotype pictures (Fordos and Gélis).*

A *hyposulphite of auric oxide and soda* appears also to be formed by dropping a neutral solution of chloride of gold into aqueous hyposulphite of soda (Fordos and Gélis).

Alloys of gold.—Gold unites with nearly all metals; but its most important alloys are those which it forms with silver and copper. Gold which is used for coins, watches, articles of jewellery, &c., is always alloyed with copper, to increase its hardness, pure gold being much too soft for any of these purposes. The standard for coin in the United Kingdom is 11 gold with 1 alloy; in France and the United States of America, 9 gold to 1 alloy. For articles of jewellery, gold is also frequently alloyed with silver, which gives it a lighter colour. The alloys of gold, both with silver and with copper, are more fusible than gold itself. The solder used for gold trinkets is composed of 5 parts gold and 1 part copper, or of 4 parts gold, 1 part copper, and 1 part silver.

Amalgam of gold.—Gold unites readily with mercury, forming a white amalgam; the smallest quantity of mercurial vapour coming in contact with gold is sufficient to turn it white. Mercury is capable of dissolving a large quantity of gold without losing its fluidity, but, when quite saturated, it acquires a waxy consistence. When the liquid amalgam is strained through chamois-leather, mercury passes through together with a very small quantity of gold, and there remains a

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* Ann. Ch. Phys. [3], xiii. 394.

white amalgam, of pasty consistence, containing about 2 parts of gold to 1 part of mercury. By dissolving 1 part of gold in 1000 parts of mercury, pressing through chamois-leather, and treating the residue with dilute nitric acid at a moderate heat, a solid amalgam, Au_8Hg, is obtained, which crystallizes in shining four-sided prisms, retains its lustre in the air, is not decomposed by boiling nitric acid, and does not melt even when heated till the mercury volatilizes (T. H. Henry).*

Gilding and silvering.—The pasty amalgam of 2 parts gold and 1 part mercury is used for gilding ornamented articles of copper and bronze. The surface of the object is first thoroughly cleaned by heating it to redness, then plunging it into dilute sulphuric acid, and sometimes for an instant also into strong nitric acid; it is then *amalgamated* by washing it with a solution of nitrate of mercury, and afterwards pressed upon the pasty amalgam, a portion of which adheres to it. The mercury is then expelled by heat, and the gold-surface finally polished. Silver may be gilt by similar processes.

By substituting an amalgam of silver for the amalgam of gold, articles of copper, bronze, and brass may be *silvered* or *plated*.

Articles of copper, chiefly copper trinkets, are also gilt by immersion in a boiling solution of chloride of gold in an alkaline carbonate, after having been cleaned by processes similar to those just described.

But the process now most generally adopted is that of *electro-gilding*, which is performed by immersing the objects to be gilt in a solution of 10 parts of cyanide of potassium and 1 part of cyanide of gold in 100 parts of distilled water, and connecting them with the negative pole of a voltaic battery, while the positive pole is connected with a bar of gold also immersed in the liquid. The solution is then decomposed by the current, the gold being deposited on the objects at the negative pole, while the gold connected with the positive pole dissolves and keeps the solution at a nearly uniform strength. The cyanide of potassium in the solution is sometimes replaced by ferrocyanide of potassium, and the cyanide of gold by sesquioxide of gold, chloride of gold and potassium, or sulphide of gold; but the composition above given is that which is most generally adopted. This mode of gilding may be at once applied to copper, brass, bronze, silver, or platinum. To gild iron, steel, or tin, it is necessary first to deposit a layer of copper on the surface, which is effected by immersion for a few seconds in a bath of cyanide of copper and potassium.

Electro-silvering or *electro-plating* is performed in a similar manner, with a bath composed of 1 part of cyanide of silver and 10 parts of cyanide of potassium dissolved in 100 parts of water; it is principally applied to articles made of nickel-silver.

Platinum may also be deposited in a similar manner on copper or silver; but it does not adhere very firmly.

ESTIMATION OF GOLD, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Gold is always estimated in the metallic state. It is generally precipitated from its solution in aqua-regia by protosulphate of iron or oxalic acid. Protosulphate of iron precipitates the gold in the form of a fine brown powder. If the gold solution is quite neutral, it must first be acidulated with hydrochloric acid, otherwise the precipitated gold will be contaminated with sesquioxide of iron formed by the action of the air on the solution of the protosulphate. If the gold solution contains much free nitric acid, there is a risk of some of the precipitated gold being re-dissolved by the aqua-regia present. To prevent this, the excess of nitric acid must be destroyed by adding hydrochloric acid, and boiling before the iron

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* Phil. Mag. [4], ix. 468.

solution is added. Oxalic acid reduces gold slowly but completely; the gold solution must be digested with it for 24 or 48 hours.

These methods of precipitation serve to separate gold from most other metals. In such cases, oxalic acid is mostly to be preferred as the precipitating agent, because, when the quantities of the other metals are also to be determined, the presence of a large amount of iron in solution is very inconvenient.

The separation of gold in alloys may generally be effected by dissolving out the baser metals with nitric, or sometimes with hydrochloric or sulphuric acid. When, however, the proportion of gold is considerable, it may happen that the alloy is but very slowly attacked by nitric acid, especially if the other metal be silver or lead. In such a case, it is best to treat the alloy with aqua-regia, and precipitate the gold with oxalic acid. Or, again, the alloy may be fused with a known weight of lead or silver, as in the method of quartation (p. 602), and thereby rendered decomposable by nitric acid.

The analysis or *assay* of an alloy of gold and copper is usually made by cupellation with lead. The weight of the button remaining on the cupel gives directly the amount of gold in the alloy after certain corrections similar to those required in the case of silver (p. 601). Alloys containing both silver and copper are cupelled with lead and a quantity of silver sufficient to bring the proportion of gold and silver in the alloy to 1 part gold and 3 parts silver. The button obtained by cupellation then consists of an alloy of gold and silver, from which the silver may be dissolved out by nitric acid.

Small ornamental articles, which would be destroyed if submitted to any of the preceding processes, are approximately assayed by rubbing them on a peculiar kind of black stone, called the *touchstone*, so as to leave a streak of metal, the appearance of which may be compared with that of similar streaks produced from alloys of known composition. A further comparison is obtained by examining the appearance which the streaks present when treated with acids. This method is also sometimes used in the assaying of coins, to afford an indication of the quantity of silver required in the cupellation. The touchstone, which is a peculiar kind of bituminous quartz, was originally obtained from Lydia; but stones of similar quality are now found in Bohemia, Saxony, and Silesia.

ORDER IX.

METALS IN NATIVE PLATINUM.

SECTION I.

PLATINUM.

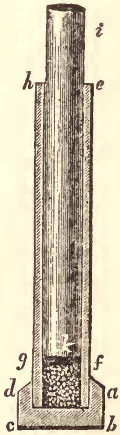
Eq. 98·68 *or* 1233·5; Pt.

This metal was discovered in the auriferous sand of certain rivers in America. Its name is a diminutive of *plata*, silver, and was applied to it on account of its whiteness. It occurs in the form of rounded or flattened grains of a metallic lustre. It has been found in Brazil, Colombia, Mexico, St. Domingo, and on the eastern declivity of the Ural chain; in small quantity also in certain copper-ores from the Alps; it is everywhere associated with the debris of a rock, easily recognised as belonging to one of the earliest volcanic formations.

The grains of native platinum contain from 75 to 87 per cent. of that metal, a quantity of iron generally sufficient to render them magnetic, from ½ to 1 per cent. of palladium, but sometimes much less, with small quantities of copper, rhodium, osmium, iridium, and ruthenium. To separate the platinum from these bodies, the ore is digested in a retort with hydrochloric acid, to which additions of nitric acid are made from time to time. When the hydrochloric acid is nearly saturated, the liquid is evaporated in the retort to a syrup, then diluted with water, and drawn off from the insoluble residue. If the mineral is not completely decomposed, more aqua-regia is added and the distillation continued. A portion always remains undissolved, consisting of grains of a compound of osmium and iridium, and little brilliant plates of the same alloy, besides foreign mineral substances which may be mixed with the ore. The solution is generally deep red, and emits chlorine from the presence of perchloride of palladium; to decompose which the liquid is boiled, whereupon chlorine escapes, and the palladium is reduced to protochloride. Chloride of potassium is then added, which precipitates the platinum as a sparingly soluble double chloride of platinum and potassium, which has a yellow colour if pure, but red if it is accompanied by the double chloride of iridium and potassium. The precipitate is collected on a filter, and washed with a dilute solution of chloride of potassium. By igniting this double salt with twice its weight of carbonate of potash to the point of fusion, the platinum is reduced to the metallic state, while a portion of the iridium remains as peroxide. The soluble potash-salts are then removed by washing with hot water, and the platinum is dissolved by aqua-regia, in which the peroxide of iridium remains untouched. To complete the separation of the iridium, the precipitation by chloride of potassium and ignition with carbonate of potash may require to be repeated several times. The platinum-solution thus freed from iridium is mixed with sal-ammoniac, which throws down a yellow precipitate of the double chloride of platinum and ammonium. From this precipitate, when heated to redness, chlorine and sal-ammoniac are given off, and the platinum remains in the form of a loosely coherent mass, called *spongy platinum.* When it is not required to have platinum absolutely pure, the solution first obtained from the ore is precipitated by sal-ammoniac, and the precipitate treated in the manner just described: much of the platinum of commerce is obtained in that way. The small trace of iridium which is left in commercial platinum greatly increases its hardness and tenacity.

Platinum is too refractory to be fused in coal furnaces: but at a high temperature its particles cohere like those of iron, and it may, like that metal, be welded, and thereby rendered malleable. For this purpose, the spongy platinum obtained by igniting the double chloride of platinum and ammonium, is introduced into a brass cylinder *e f g h* (fig. 205), the lower part of which fits into a steel socket *a b c d.* The cylinder being half filled with spongy platinum, a steel piston *i k*, which fits it exactly, is introduced, and driven down by blows of a hammer, gently at first, but afterwards with greater force. The spongy platinum is thereby much reduced in bulk, and after a while is converted into a coherent disc of metal. This disc is heated to whiteness in a muffle, and afterwards hammered on a steel anvil. By repeating these operations several times, the platinum is rendered perfectly malleable and ductile, and may be rolled into sheets. Platinum in this state is the densest body at present known; its specific gravity was fixed by Dr. Wollaston at 21.53. This metal may be fused by the oxyhydrogen blow-pipe, or even made to boil, and be dissipated with scintillations. It is not acted upon by any single acid, not even by concentrated and boiling sulphuric acid. Its resistance to the action of acids, conjoined with its difficult fusibility, renders platinum invaluable for chemical experiments, and for some purposes in the chemical arts, particularly for the concentration of oil of vitriol.

FIG. 205.



The remarkable influence of a clean surface of platinum in determining the combustion of oxygen and hydrogen, has already been considered. This property platinum shares with osmium, iridium, palladium, and rhodium. It is exhibited in the greatest degree by the highly divided metal, such as platinum-sponge, the condition in which the metal is left on igniting the double chloride of platinum and ammonium. Platinum precipitated from solution by zinc, causes the combustion of alcohol vapour. The *black powder of platinum*, commonly called *platinum-black*, is the form in which that metal is most active. This is prepared by dissolving the protochloride of platinum in a hot and concentrated solution of potash, and pouring alcohol into it while still hot, by small quantities at a time; violent effervescence then occurs from the escape of carbonic acid gas, by which the contents of the vessel, unless capacious, may be thrown out. The liquor is decanted from the black powder which appears, and the latter boiled successively with alcohol, hydrochloric acid, and potash, and finally four or five times with water, to divest it of all foreign matters. Platinum-black may also be obtained by decomposing a hot solution of sulphate of platinum with alcohol; and by boiling a solution of the bichloride with carbonate of soda and sugar; chloride of sodium is then formed, water and carbonic acid are produced by oxidation of the sugar, and the platinum is precipitated in the finely-divided state. The powder, when dried, resembles lamp-black, and soils the fingers, but still it is only metallic platinum extremely divided, and may be heated to full redness without any change of appearance or properties. It loses these properties, however, by the effect of a white heat, and assumes a metallic aspect. Platinum-black, like wood charcoal, absorbs and condenses gases in its pores, with evolution of heat, a property which must assist its action on oxygen and hydrogen, although not essential to that action. When moistened with alcohol, it determines the oxidation of that substance in air, and the formation of acetic acid; and, in a similar manner, it converts wood-spirit into formic acid.

Platinum is insoluble in all acids except aqua-regia. It may be oxidated in the dry way by fusing it with hydrate of potash or nitre. Palladium, osmium, and iridium resemble platinum in their chemical relations, the corresponding compounds of these four metals being isomorphous; platinum and iridium have also the same atomic weight. Of platinum, only two degrees of oxidation are known with certainty, the protoxide, PtO, and binoxide, PtO_2.

Protoxide of platinum, Platinous oxide, PtO, 106·68 *or* 1333·5.—This oxide is obtained by digesting the corresponding chloride of platinum with potash, as a black powder, which is a hydrate. It is dissolved by an excess of the alkali, and forms a green solution, which may become black like ink with a large quantity of oxide. Protoxide of platinum forms the platinous class of salts, which have a greenish, or, sometimes red colour, and are distinguished from the platinic salts by not being precipitated by sal-ammoniac. With *hydrosulphuric acid* and *hydrosulphate of ammonia*, they form a black precipitate, soluble in a large excess of the latter; with *mercurous nitrate*, a black precipitate; with *potash*, no precipitate; with *carbonate of potash or soda*, a brownish precipitate. *Ammonia* added to the hydrochloric acid solution throws down a green crystalline precipitate of ammonio-platinous chloride; carbonate of ammonia forms no precipitate.

Protosulphide of platinum, PtS, is thrown down as a black precipitate, when the protochloride of platinum is decomposed by hydrosulphuric acid. It may be washed and dried without decomposition.

Protochloride of platinum, Platinous chloride, PtCl, is obtained by evaporating a solution of the bichloride of platinum to dryness; triturating the dry mass; and heating it in a porcelain capsule by a sand-bath at the melting point of tin, taking care to stir it at the same time, so long as chlorine is evolved. It remains as a greenish grey powder, quite insoluble in water, and repelling that liquid so as not to be moistened by it. This chloride is not decomposed by sulphuric or nitric acid, but is partially soluble in boiling and concentrated hydrochloric acid. From the last solution, alkalies throw down a black precipitate of protoxide. When the calcination of the bichloride of platinum, at 420° or 460°, is interrupted before the whole of the chlorine is expelled, the residue yields to water a compound of a brown colour, so deep, that the liquid becomes opaque. This, Professor Magnus believes to be a combination of the two chlorides of platinum. A double *protochloride of platinum and potassium*, or *chloroplatinite of potassium*, $PtCl \cdot KCl$, is obtained on adding chloride of potassium to the solution of platinous chloride in hydrochloric acid, and evaporating the liquid. The salt crystallizes in red four-sided prisms, the form of which is the same as that of a corresponding salt of palladium; it is anhydrous. A protochloride of platinum and sodium also exists, but does not crystallize easily.

Corresponding *platinous iodides* and *cyanides* have been formed. The cyanide forms a numerous class of double salts, called *platinocyanides*, whose general formula is $MCy.PtCy$. The potassium salt is obtained by heating spongy platinum with ferrocyanide of potassium; exhausting the mass with hot water and crystallizing; or by treating platinous chloride with aqueous cyanide of potassium. The salt crystallizes in needles and rhombic prisms, pale yellow by transmitted light, yellow or blue by reflected light, according to the direction in which they are viewed. From the solution of this salt, the platino-cyanides of zinc, lead, copper, mercury, and silver, which are insoluble, are obtained by precipitation. The sodium, barium, strontium, and calcium-salts, which are soluble, are obtained by treating the copper-salt with caustic soda, baryta, &c.; and the magnesium and aluminum-salts, by precipitating the barium-salt with sulphate of magnesia or alumina. The ammonium-salt is prepared like the potassium-salt. Platinous oxide has also been united with several acids, particularly sulphuric, nitric, oxalic, and acetic acids; but none of these salts have been crystallized except the oxalate.

Bioxide of platinum, Peroxide of platinum, Platinic oxide, PtO_2, 114·68 *or* 1433·5.—By precipitating sulphate of platinum with nitrate of baryta, nitrate of platinum is obtained. One half of its oxide may be precipitated by soda, from the last salt, but when a larger quantity of alkali is added, a subsalt is thrown down. The precipitated oxide is hydrated, very bulky, and exactly resembles sesquioxide of iron precipitated by ammonia. When heated, it first loses its water, and becomes black, then its oxygen, and leaves metallic platinum. Bioxide of platinum combines with acids, and forms a class of salts, which are either yellow or reddish-brown. From the solutions of these salts, the platinum is precipitated in the metallic state by *phosphorus* and by most *metals*. *Hydrosulphuric acid* and *sulphide of ammonium* form a black precipitate soluble in a large excess of the latter. In a solution of platinic chloride, *potash* or *ammonia* forms a yellow crystalline precipitate of chloroplatinate of potassium or ammonium; so likewise do the *chlorides of potassium* or *ammonium*; sodium-salts form no precipitate. In the solution of platinic nitrate or sulphate, *potash* or *ammonia* forms a yellow-brown precipitate; *chloride of potassium* or *ammonium* produces, after some time, a slight yellow precipitate of the double chloride. Platinic oxide has also a decided affinity for bases, and forms insoluble compounds with the alkalies, earths, and many metallic oxides. It forms also, like sesquioxide of gold, a fulminating ammoniacal compound, discovered by Mr. E. Davy.

Bisulphide of platinum, PtS_2, is formed by adding a solution of bichloride of platinum, drop by drop, to a solution of sulphide of potassium. It is a dark brown and becomes black by desiccation. When dried in open air, a portion of its sulphur is converted into sulphuric acid, by absorption of oxygen, and the mass becomes strongly acid.

Bichloride of platinum, $PtCl_2$, 2121 *or* 169·68, is obtained by concentrating the solution of platinum in aqua-regia, as a red saline mass, which becomes brown when deprived of its water of crystallization by heat. The solution of this salt when pure has an intense and unmixed yellow colour, the red colour which it usually exhibits being due to iridium or to protochloride of platinum. Bichloride of platinum is soluble in alcohol, and the solution is used to separate potash and ammonia in analysis.

Chloride of platinum and potassium, Chloroplatinate of potassium, $KCl \, . \, PtCl_2$, is the salt which falls on mixing chloride of platinum with chloride of potassium or any other salt of potash. The crystalline grains of which it is composed are regular octohedrons. This salt is soluble to a certain extent in water, but is wholly insoluble in alcohol. It is anhydrous. A very intense red-heat is required for its complete decomposition. *Chloroplatinate of sodium*, $NaCl \, . \, PtCl_2+6HO$, crystallizes in beautiful transparent prisms of a bright yellow colour. It is soluble in alcohol as well as in water. When a solution of this salt in alcohol is distilled till only one-fourth of the liquid remains, the solution yields by evaporation a salt containing the elements of ether, and belonging to a class of compounds discovered by Professor Zeise, and known as the etherized salts of Zeise.

Chloroplatinate of ammonium resembles the double salt of potassium. When ignited, it leaves metallic platinum in the spongy state. Bonsdorff has formed a large class of compounds of bichloride of platinum with the alkaline, earthy, and metallic chlorides, in all of which the salts are united in single equivalents. The bromides and iodides of platinum have likewise been formed, and classes of double salts derived from them. Bioxide of platinum has also been combined with acids; but none of its salts, with the exception of the oxalate, is obtained in a crystalline state.

Bicyanide of platinum, or *platinic cyanide*, does not appear to exist in the separate state; but it forms double salts with the cyanides of potassium and ammonium; it likewise combines with chloride of potassium, forming the compound $KCl \, . \, PtCy_2$.

The *sulphocyanides of platinum*, $PtCyS_2$, and $Pt \, . \, (CyS_2)_2$, likewise form two series of double salts, viz., the *platino-bisulphocyanides* or *sulphocyanoplatinites* $= MPt(CyS_2)_2$, or $MCyS_2+PtCyS_2$, and the *platino-tersulphocyanides* or *sulphocyanoplatinates* $= MPt(CyS_2)_3$, or $MCyS_2=Pt(CyS_2)_2$. The potassium salts are formed by the action of sulphocyanide of potassium on protochloride and bichloride of platinum respectively. All these salts are strongly coloured, exhibiting all shades of colour from light yellow to deep red. They are quickly decomposed by heat (G. B. Buckton).[*]

AMMONIACAL PLATINUM SALTS.

The oxides, chlorides, sulphates, &c., of platinum are capable of taking up the elements of 1 or 2 equivalents of ammonia, giving rise to four series of compounds, whose composition may be represented by the following general formulæ, in which the symbols R, R′ denote acid elements:

1. Ammonio-platinous compounds, or protosalts of platammonium,

$$NH_3PtR = \overbrace{NH_3Pt} \, . \, R.$$

2. Biammonio-platinous compounds, or protosalts of ammo-platammonium,

$$N_2H_6PtR = \overbrace{NH^2(NH_4)Pt} \, . \, R.$$

3. Ammonio-platinic compounds, or bisalts of platammonium,

$$NH_3Pt\left\{\begin{matrix} R_2 \\ \text{or } RR' \end{matrix}\right. = \overbrace{NH_3Pt} \, . \left\{\begin{matrix} R_2 \\ \text{or } RR'. \end{matrix}\right.$$

4. Biammonio-platinic compounds, or bisalts of ammo-platammonium,

$$N_2H_6Pt\left\{\begin{matrix} R_2 \\ \text{or } RR' \end{matrix}\right. = \overbrace{NH_2(NH_4)Pt} \, . \left\{\begin{matrix} R_2 \\ \text{or } RR'. \end{matrix}\right.$$

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[*] Chem. Soc. Qu. J. vii 22.

The third and fourth classes of these compounds may also be regarded as protosalts of compound ammoniums, in which 1 eq. of hydrogen is replaced by PtO or PtCl: for example, the bichloride $NH_3PtCl_2 = \overbrace{NH_3(PtCl)} . Cl$; the chloronitrate $N_2H_6PtClNO_6 = \overbrace{NH_2(NH_4)PtCl} . NO_6$.

1. *Ammonio-platinous compounds, or Protosalts of Platammonium.* — These compounds are formed by the action of heat on those of the following series, half the ammonia of the latter being then given off. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the biammoniacal platinous compounds; they detonate when heated.

Oxide, $NH_3PtO = \overbrace{NH_3Pt} . O$. — Obtained by heating the hydrated oxide of biammo-platammonium to 230°. It is a greyish mass which, when heated to 392° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. Probably the compound, Pt_3N, is first produced and is afterwards resolved into nitrogen and platinum:

$$3NH_3PtO = Pt_3N + 3HO + 2NH_3.$$

The oxide, heated to 392° in contact with the air, becomes incandescent, and burns vividly, leaving a residue of platinum.

Chloride, $NH_3PtCl = \overbrace{NH_3Pt} . Cl$.—Of this compound three isomeric modifications exist: *α*. *Yellow*, obtained by adding hydrochloric acid, or a soluble chloride, to a solution of nitrate or sulphate of platammonium. Or, by boiling the green modification, γ, with nitrate or sulphate of ammonia, whereupon it dissolves and forms a solution which, on cooling, deposits the yellow salt. Or, by neutralizing a solution of platinous chloride in hydrochloric acid with carbonate of ammonia, heating the mixture to the boiling point, and adding a quantity of ammonia equal to that already contained in the liquid, filtering from a dingy green substance, which deposits after a while, then leaving the solution to cool, and decanting the supernatant liquid as soon as the yellow salt is deposited. β. *Red.*—If, in the last mode of preparation, the carbonate of ammonia, instead of being added at once in excess, be added drop by drop to the hydrochloric acid solution of platinous chloride, the liquid on cooling deposits small garnet-coloured crystals having the form of six-sided tables. This red modification may also be obtained in other ways (Peyrone).* *γ*. *Green.* — This modification, usually denominated the *green salt of Magnus*, was the first discovered of the ammoniacal platinum compounds. It is obtained by gradually adding an acid solution of platinous chloride to caustic ammonia, or by passing sulphurous acid gas into a boiling solution of bichloride of platinum till it is completely converted into protochloride (and therefore no longer gives a precipitate with sal-ammoniac), and neutralizing the solution with ammonia; the compound is then deposited in green needles. The same modification of the salt may also be obtained by adding an acid solution of platinous chloride to a solution of biammonio-platinous chloride, N_2H_6PtCl. Hence it would appear that the true formula of this green salt is $(NH_3PtCl)_2 = PtCl + \overbrace{NH_2(NH_4)Pt} . Cl$, that of the yellow or red modification being simply NH_3PtCl. Either modification of the salt, when heated to 572°, gives off nitrogen, hydrochloric acid, and sal-ammoniac, and leaves a residue of platinum.

A red crystalline compound of chloride of platammonium with chloride of ammonium, viz. $NH_3PtCl + NH_4Cl$, is formed when a solution of chloride of ammoplatammonium, containing a large quantity of sal-ammoniac, is evaporated to the crystallizing point. Thus, when a solution of platinous chloride in hydrochloric acid is precipitated by ammonia, and the green salt of Magnus thereby formed is

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* Vide Translation of Gmelin's Handbook, vi. 303.

heated, while still in the liquid, with excess of ammonium, to convert it into chloride of ammo-platammonium, the red compound separates at a certain degree of concentration, together with the chloride of ammo-platammonium (Grimm.)*

Iodide, NH_3PtI. — Yellow powder, obtained by boiling the aqueous solution of the compound N_2H_6PtI. It dissolves in ammonia, and is thereby reconverted into the latter compound.

Cyanide, NH_3PtCy. — Obtained by adding hydrocyanic acid to a solution of biammonio-platinous oxide, cyanide of ammonium being formed at the same time (Reiset):

$$N_2H_6PtO + 2HCy = NH_3PtCy + NH_4Cy + HO.$$

Also, by digesting ammonio-platinous chloride with cyanide of silver. It crystallizes in fine regular needles of a pale yellow colour, soluble with tolerable facility in water and ammonia. An isomeric modification of this compound, $(NH_3PtCy)_2 = N_2H_6PtCy + PtCy$, is formed by passing cyanogen gas into a moderately concentrated solution of biammonio-platinous oxide; the cyanogen then decomposes the water, forming hydrocyanic and cyanic acids, and the hydrocyanic acid acts upon the biammonio-platinous oxide, forming the compound $(NH_3PtCy)_2$, together with ammonia and water:

$$2(N_2H_6PtO) + 2HCy = (NH_3PtCy)_2 + 2NH_3 = 2HO.$$

The compound, $(NH_3PtCy)_2$, crystallizes out and may be purified by recrystallization from water. It is also obtained by mixing a solution of biammonia-platinous chloride with cyanide of potassium. It forms crystals which, under the microscope, appear like six-sided tables arranged in stellate groups; it dissolves without decomposition in potash, hydrochloric acid, and dilute sulphuric acid, but is decomposed by strong sulphuric and by nitric acids (Buckton).†

The sulphate, $NH_3Pt.SO_4.HO$, and the *nitrate*, $NH_3Pt.NO_6$, are obtained by boiling the iodide with sulphate and nitrate of silver; they are crystalline, and have a strong acid reaction. The sulphate retains one atom of water, which cannot be removed without decomposing the salt.

2. *Biammonio-platinous compounds, or Protosalts of Ammo-platammonium.*— *Oxide*, $N_2H_6PtO\,.\,HO = N\overbrace{H_2(NH_4)Pt}\,.\,O + HO$. — Obtained by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in vacuo; a crystalline mass is then left, containing $N_2H_6PtO\,.\,HO$. The oxide is not known in the anhydrous state. The hydrate is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates oxide of silver from the solution of the nitrate. It is a strong base, neutralizing acids completely, and expelling ammonia from its salts. It melts at 230°, giving off water and ammonia, and leaving the compound NH_3PtO. Its aqueous solution does not give off ammonia, even when boiled.

Chloride, $N_2H_6PtCl = N\overbrace{H_2\,(NH_4)\,Pt}\,.\,Cl$.—This compound is prepared by boiling protochloride of platinum, or the green salt of Magnus, with aqueous ammonia, till the whole is dissolved, and evaporating the liquid to the crystallizing point. Or, by passing sulphurous acid gas into bichloride of platinum till the solution is completely decolourized, precipitating with carbonate of soda, dissolving the precipitate of sodio-platinous sulphite in hydrochloric acid, saturating the resulting solution of chloride of sodium and platinous chloride with ammonia, and dissolving the precipitate of N_2H_6PtCl and NH_3PtCl in boiling hydrochloric acid. The filtered liquor on cooling deposits NH_3PtCl, while the biammoniacal compound remains in solution and may be obtained by evaporation, mixed however, with salammoniac. It separates in bulky crystals of a faint yellow colour, containing 1 eq.

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* Ann. Ch. Pharm. xcix. 95.

† Chem. Soc. Qu. J. iv. 34.

water, which is completely given off at 230°. At 482° it gives off ammonia, and leaves NH_3PtCl. The anhydrous compound rapidly absorbs water from the air. The hydrate does not give off ammonia when treated with caustic alkalies in the cold, and is but very slowly decomposed by them, even with the aid of heat.

Chloride of ammoplatammonium forms two compounds with bichloride of platinum. The first, whose formula is $2(\overbrace{NH_2(NH_4)\,Pt}\,.\,Cl) + PtCl_2$, is obtained as an olive-green precipitate on adding bichloride of platinum to a solution of $\overbrace{NH_2(NH_4)Pt}\,.\,Cl$; the second, $\overbrace{NH_2(NH_4)Pt}\,.\,Cl + PtCl_2$, by treating the preceding with excess of bichloride of platinum.

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium; they crystallize in cubes.

The *sulphate*, $\overbrace{NH_2\,(NH_4)\,Pt}\,.\,SO_4$, and the *nitrate* $NH_2(NH_4)Pt.NO_6$, are obtained by decomposing the chloride with sulphate or nitrate of silver; they are neutral, and crystallize easily.

Carbonates. — The hydrated oxide absorbs carbonic acid rapidly from the air, forming first, a neutral carbonate, $\overbrace{NH_2(NH_4)\,Pt}\,.\,CO + HO$, and afterwards an acid salt, $\overbrace{NH_2\;(NH_4)\;Pt}\,.\,CO_3 + CO_3H$.

3. *Ammonio-platinic compounds; or, Bi-salts of platammonium.*—The *oxide*, $NH_3PtO_2 = \overbrace{NH_3Pt}\,.\,O_2$, may also be regarded as *oxide of oxyplatammonium*, $\overbrace{NH_3(PtO)}\,.\,O$. It is obtained by adding ammonium to a boiling solution of ammonio-platinic nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small, shining, rhomboidal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic acid, and forms a large number of crystallizable salts, both neutral and acid, having a yellow colour, and sparingly soluble in water (Gerhardt).* Another compound of platinic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing chloroplatinate of ammonium with aqueous potash. It is a straw-coloured powder, which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

Chloride, $NH_3PtCl_2 = \overbrace{NH_3Pt}\,.\,Cl_2 = \overbrace{NH_3(PtCl)}\,.\,Cl$. — Obtained by passing chlorine gas into boiling water in which the compound NH_3PtCl (the yellow modification) is suspended. This compound is insoluble in cold water, and very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of biammoniacal platinic chloride. The compound $NH_3Pt.Cl_2$ dissolves in boiling potash without evolving ammonia. An isomeric compound,

$$(NH_3PtCl_2)_2 = N_2H_6PtCl_2 + PtCl_2,$$

is obtained by passing chlorine into water in which Magnus's green salt is suspended. A red crystalline powder is at first precipitated, consisting of $N_2H_6PtCl + PtCl_2$; but on continuing the passage of the chlorine, this precipitate redissolves, and the solution yields, by evaporation, the crystalline compound $(NH_3PtCl_2)_2$.

The *sulphate*, $NH_3Pt.(SO_4)_2$, is obtained by dissolving the oxide in dilute sulphuric acid, and evaporating. It is a yellow powder, having an acid taste, and is soluble in boiling water.

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* Comptes Rendus des Travaux de Chimie, 1849, p. 273.

Nitrates. — A *mononitrate*, $NH_3PtO_2.NO_5 + 3HO$, or *oxynitrate*, $\overbrace{NH_3Pt}.\left\{\begin{matrix}NO_6\\O\end{matrix}\right. + 3HO$, or *nitrate of oxyplatammonium*, $\overbrace{NH_3(PtO)}.NO_6 + 3HO$ is obtained by boiling the chloride NH_3PtCl_2 for several hours with a dilute solution of nitrate of silver. It is a yellow, crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *binitrate*, $\overbrace{NH_3Pt}.2NO_6 + 2HO$, is obtained by dissolving the mononitrate in nitric acid; it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxalate*, $NH_3PtO_2.C_2O_3 + 2HO$, or $NH_3Pt\left\{\begin{matrix}C_2O_4\\O\end{matrix}\right. + 2HO$, or $\overbrace{NH_3(PtO)}.C_2O_4 + 2HO$, is formed by decomposing the nitrate with oxalate of ammonia. It is a light yellow precipitate, soluble in boiling water, and detonating when heated.

4. *Biammonio-platinic compounds*, or *Bi-salts of ammoplatammoninum.*—The oxide of this series has not yet been isolated.

Chloride.—$N_2H_6PtCl_2 = \overbrace{NH_2(NH_4)Pt.}Cl_2 = \overbrace{NH_2(NH_4)(PtCl)}.Cl$.—Obtained by passing chlorine gas into a solution of biammonio-platinous chloride, N_2H_6PtCl; by dissolving ammonio-platinic chloride, NH_3PtCl_2, in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of one of the nitrates,

$$N_2H_6PtO_2.NO_5, \text{ or } N_2H_6PtClO.NO_5,$$

with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent, regular octohedrons, having a faint yellow tint. When a solution of this salt is treated with nitrate of silver, one half of the chlorine is very easily precipitated, but to remove even a small portion of the remainder requires a long-continued action of the silver-salt; a result easily explained if the salt be regarded as a chloride of ammo-chlorplatammonium, $\overbrace{NH_2(NH_4)(PtCl)}.Cl$ (Grimm.)* A compound having the formula N_2H_5PtCl, containing, therefore, 1 eq. Cl and 1 eq. H less than the preceding, is obtained by dissolving chloroplatinate of ammonium in ammonia, and precipitating by alhocol; but it does not crystallize, merely drying up to a pale yellow, resinous mass: hence its composition is doubtful.

Nitrates.—A mononitrate, $N_2H_6PtO_2.NO_5$, or oxynitrate of ammoplatammonium, $\overbrace{NH_2(NH_4)Pt}\left\{\begin{matrix}NO_6\\O\end{matrix}\right.$, or nitrate of ammoxyplatammonium, $\overbrace{NH_2(NH_4)(PtO)}.NO_6$, is obtained by boiling the following salt *b*, with ammonia: it is a white amorphous powder, slightly soluble in cold, more soluble in boiling water.

Sesquinitrate, $2(N_3H_6PtO_2).3NO_5$, or

$$2\left(\overbrace{NH_2(NH_4)Pt}\right).\left\{\begin{matrix}3NO_6\\O\end{matrix}\right., \text{ or } \left.\begin{matrix}\overbrace{NH_2(NH_4)(PtO)}\\\overbrace{NH_2(NH_4)(PtNO_6)}\end{matrix}\right\}2NO_6.—$$

Formed by boiling the mononitrate of ammoplatammonium with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid (Gerhardt).

Chloronitrates. — *a.* $N_2H_6PtClO.NO_5$; or $\overbrace{NH_2(NH_4)Pt.}\left\{\begin{matrix}NO_6\\Cl,\end{matrix}\right.$ or $\overbrace{NH_2(NH_4)(PtCl)}.NO_6$. — This salt was discovered by Gros. It is obtained by treating Magnus's green salt with strong nitric acid. The green compound first turns brown, and is afterwards converted into a mixture of platinum and a white powder, which is dissolved out by boiling water, and

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* Ann. Ch. Pharm. xcix. 77

crystallizes on cooling in shining flattened prisms, colourless, or having a pale yellow tint. The reaction may be thus represented:—

$$2(NH_3PtCl) + HO.NO_5 = N_2H_6PtCl.NO_6 + Pt + HCl.$$

This compound dissolves readily in water, especially when heated. The chlorine and platinum contained in the solution cannot be detected by the ordinary reagents; thus, nitrate of silver and hydrosulphuric acid yield but very trifling precipitates, even after a long time.

$$b.\ 4NH_3.Pt_2ClO_3.2NO_5,\ \text{or}\ \left.\begin{matrix} N\overbrace{H_2(NH_4)\ (PtCl)} \\ N\overbrace{H_2(NH_4)\ (PtCl)} \end{matrix}\right\}.\ 2NO_6.$$

Discovered by Raewsky. When Magnus's green salt is boiled with a large excess of nitric acid, red fumes are evolved, and the resulting solution deposits this salt in small, brilliant, needle-shaped prisms, which deflagrate when heated, giving off water and chloride off ammonium, and leaving metallic platinum. Raewsky assigns to this salt the formula $4NH_3.Pt_2ClO_5.2NO_5$; but the formula above given, which is deduced from Gerhardt's analysis, and contains 2O less, is much more probable, as it accords with the constitution of the other compounds of the series. The 2 atoms of nitric acid contained in this salt may be replaced by 2 atoms of *carbonic* or *oxalic* acid, yielding sparingly soluble crystalline salts of exactly similar constitution. There is also a *phosphate* containing $4NH_3.Pt_2ClO_3.PO_5.HO$, obtained by mixing the solution of the nitrate with ordinary phosphate of soda. According to Raewsky, the mother-liquor from which the preceding nitrate has crystallized, contains another nitrate whose formula is $4NH_3.Pt_2Cl_2O_4.2NO_5$; but Gerhardt finds this salt to be identical with the nitrate discovered by Gros.

Chlorosulphate, $N_2H_6PtClSO_4 = N\overbrace{H_2\ (NH_4)\ (PtCl)}\ .\ SO_4$.—Obtained by treating biammonio-platinic chloride, or Gros's nitrate, with dilute sulphuric acid, or by mixing the solution of the nitrate with a strong solution of a soluble sulphate. It crystallizes in slender needles, sparingly soluble in cold water, but dissolving with tolerable facility in boiling water. The sulphuric acid in the solution is not precipitated by baryta-salts. The salt is, however, decomposed by hydrochloric or nitric acid, either of which takes the place of the sulphuric acid, reproducing the chloride or nitrate (Gros).

Chloroxalate, $N_2H_6PtClO.C_2O_3 = N\overbrace{H_2(NH_4)Pt}\left\}\begin{matrix} C_2O_4 \\ Cl \end{matrix}\right. = N\overbrace{H_2(NH_4)(PtCl)}.C_2O_4.$

Oxalic acid or an alkaline oxalate added to the solution of the corresponding sulphate or nitrate, throws down this salt in the form of a white granular precipitate, insoluble in water.

Oxalonitrates.—*a.* $N_2H_6PtO_2.NO_5.C_2O_3 =$

$$N\overbrace{H_2(NH_4)Pt}.\left\{\begin{matrix} NO_6 \\ C_2O_4 \end{matrix}\right. = N\overbrace{H_2(NH_4)(PtNO_6)}.C_2O_4.$$

Deposited as a white crystalline body from a solution of the following salt *b* in dilute nitric acid.

$$b.\ 2(N_2H_6PtO_2).NO_5.2C_2O_3 = 2(N\overbrace{H_2(NH_4)Pt}).\left\{\begin{matrix} 2C_2O_4 \\ NO_6 \\ O \end{matrix}\right. =$$

$\left.\begin{matrix} N\overbrace{H_2(NH_4)PtO} \\ NH_2(NH_4)(PtNO_6) \end{matrix}\right\} 2C_2O_4$. — Obtained by adding oxalate of ammonia to a solution of the sesquinitrate; it is insoluble in water (Gerhardt).

GERHARDT'S THEORY OF THE AMMONIACAL PLATINUM COMPOUNDS.

These compounds may be regarded as salts of peculiar bases or alkalies, formed from ammonia by the substitution of one or two atoms of platinum for hydrogen; admitting, however, that platinum (like other metals) may enter into its compounds with two different equivalent weights, viz., in the platin*ous* compounds, as *Platinosum* $=98{\cdot}68=\mathrm{Pt}$, and in the platin*ic* compounds, as *Platinicum* $=49{\cdot}34=\mathrm{pt}$. This being admitted, the ammonio-platinous compounds may be regarded as salts of an alkali, called *Platosamine* $=NH_2Pt$, formed from ammonia by the substitution of 1 atom of platinosum for 1 atom of hydrogen; and the biammonio-platinous compounds, as salts of *Diplatosamine* $=N_2H_5Pt$, formed by the union of two atoms of ammonia into one, and the substitution therein of 1 Pt for 1 H: thus for the chlorides:—

NH_3PtCl = Hydrochlorate of Platosamine $= NH_2Pt.HCl$;
N_2H_6PtCl = Hydrochlorate of Diplatosamine $= N_2H_5Pt.HCl$;

and for the nitrates:—

$NH_3Pt.NO_6$ = Nitrate of Platosamine $= NH_2Pt.HNO_6$;
$N_2H_6Pt.NO_6$ = Nitrate of Diplatosamine $= N_2H_5Pt.HNO_6$.

In a similar manner, the ammonio-platinic compounds may be regarded as salts of *Platinamine* $= NHpt_2$, and the biammonio-platinic compounds as salts of *Diplatinamine* $=N_2H_4pt_2$; thus—

NH_3PtCl_2 = Bihydrochlorate of Platinamine $= NHPt_2.2HCl$.
$N_2H_6PtCl_2$ = Bihydrochlorate of Diplatinamine $= N_2H_4pt_2.2HCl$.

Diplatinamine forms three kinds of salts, viz., mono-acid, sesqui-acid, and bi-acid salts; and, moreover, exhibits a peculiar tendency to form double salts containing two acids: thus, the salts discovered by Gros may be regarded as bi-acid salts, and those discovered by Raewsky, as sesqui-acid salts of diplatinamine containing hydrochloric together with another acid; thus:—

Mononitrate $= N_2H_6PtO_2.NO_5 = N_2H_4pt_2.HNO_6 + HO$.
Sesquinitrate $= 2(N_2H_6PtO_2).3NO_5 = 2N_2H_4pt_2.3HNO_6 + HO$.

$$\left.\begin{matrix}\text{Chloronitrate}\\ \text{(Gros's nitrate)}\end{matrix}\right\} = N_2H_6PtClO.NO_5 = N\,H_4pt_2.\left\{\begin{matrix}HCl\\ HNO_6\end{matrix}\right..$$

$$\left.\begin{matrix}\text{Sesquichloronitrate}\\ \text{(Raewsky's nitrate)}\end{matrix}\right\} = N_4H_{12}Pt_2ClO_3.2NO_5 = 2N_2H_4pt_2.\left\{\begin{matrix}HCl\\ 2HNO_6\end{matrix}\right. + HO.$$

$$\text{Oxalonitrate} = N_2H_6PtO_2.NO_5.C_2O_3 = N_2H_4pt_2.\left\{\begin{matrix}C_2HO_4\\ HNO_6.\end{matrix}\right.$$

$$\text{Sesqui-oxalonitrate} = 2(N_2H_6PtO_2).NO_5.2C_2O_3 = 2N_2H_4pt_2.\left\{\begin{matrix}2C_2HO_4\\ HNO_6\end{matrix}\right. + HO.$$

ESTIMATION AND SEPARATION OF PLATINUM.

For quantitative estimation, platinum is usually precipitated from its solutions in the form of chloroplatinate of ammonium. The acid solution of platinum, after sufficient concentration, is mixed with a very strong solution of sal-ammoniac, and a sufficient quantity of strong alcohol added to render the precipitation complete. The precipitate of chloroplatinate of ammonium is then washed with alcohol, to which a small quantity of sal-ammoniac has been added, and then heated to redness in a weighed porcelain crucible, whereupon it is decomposed and leaves metallic platinum. Great care must, however, be taken in the ignition to prevent loss, as the evolved vapours are very apt to carry away small particles of the salt and of the reduced metal. The best mode of avoiding this source of error is to place the precipitate in the crucible *enclosed in the filter*, and expose it for some time to a moderate heat, with the cover on the crucible, till the filter is charred, and then to a somewhat higher temperature to expel the chlorine and chloride of ammonium. The crucible is then partially opened, and the carbonaceous matter of the filter burnt away in the usual manner. When these precautions are duly observed, not a particle of platinum is lost. Instead of igniting the precipitate and weighing the platinum, the precipitate is sometimes collected on a weighed filter, dried over the water-bath and weighed; but this method is less accurate, because the precipitate always contains an excess of sal-ammoniac (H. Rose).

Chloride of potassium may also be used instead of chloride of ammonium to precipitate platinum, the concentrated solution of the platinum being previously mixed with a sufficient quantity of strong alcohol to bring the per centage of alcohol in the liquid to between 60 and 70 per cent. The precipitated chloroplatinate of potassium is then washed with alcohol of 60 to 70 per cent., and decomposed by simple ignition in a porcelain crucible, if its quantity is small, or in an atmosphere of hydrogen if its quantity is larger; the chloride of potassium washed out by water; and the platinum dried, ignited, and weighed.

Potash and ammonia may also be estimated by precipitating their solutions with chloride of platinum, and treating the precipitates in the manner just described. Every 100 parts of platinum correspond to 47·83 parts of potash, and 17·25 parts of ammonia.

The same methods of precipitation serve also for the separation of platinum from most of the preceding metals. To separate platinum from *silver*, when the two metals are combined in an alloy, the best method is to heat the alloy with pure and strong sulphuric acid, diluted with about half its weight of water, till the sulphuric acid begins to escape in dense fumes. The silver is thereby converted into sulphate, and the platinum remains behind in the metallic state. The sulphate of silver is dissolved by a large quantity of hot water, the platinum washed with hot water, and again treated with sulphuric acid, to separate the last traces of silver.

SECTION II.

PALLADIUM.

Eq. 53·36 *or* 665·9; Pd.

This metal was discovered in 1803 by Dr. Wollaston. It is precipitated by cyanide of mercury from the solution of the ore of platinum, after the removal of that metal by sal-ammoniac, and is gradually deposited as a yellowish white flocculent powder, which is cyanide of palladium, and yields the metal when calcined. Palladium likewise occurs, associated with a larger quantity of gold and a small quantity of silver, in a peculiar gold-ore from Brazil, called *oropudre.* This mineral, which contains 10 per cent. of palladium, and is the chief source of that metal, is dissolved in aqua-regia, the acid solution saturated with potash, and the palladium precipitated by cyanide of mercury.

In external characters, palladium closely resembles platinum. It is nearly as infusible, but can more easily be welded. The density of the fused metal is 11·3; after being laminated, 11·8. At a certain temperature, the surface of palladium tarnishes and becomes blue from oxidation, but at a stronger heat the oxide is reduced. Palladium is very slightly attacked by boiling and concentrated hydrochloric and sulphuric acids. It dissolves in nitric acid, communicating a brownish red colour to the acid, while no gas is evolved if the temperature is low, the nitric acid being converted into nitrous acid. Palladium dissolves with facility in aqua-regia; its surface is blackened by tincture of iodine, which has no effect upon platinum.

Palladium is sometimes used for making the divided scales of astronomical instruments; being nearly as white as silver, and not blackened by sulphurous emanations, it is well adapted for that purpose. An alloy of palladium with 1-10th of its weight of silver is used by dentists.

Palladium has a much greater affinity for oxygen than platinum. It forms two oxides, the *protoxide* PdO, and the *bioxide* PdO_2.

Protoxide of palladium, Palladous oxide, PdO, 61·27 *or* 765·9.—This oxide is obtained by dissolving palladium in nitric acid, evaporating the solution to dryness, and calcining the nitrate at a gentle heat. It forms a black mass, which dissolves with difficulty in acids. When carbonate of potash or soda is added in excess to a palladous salt, the hydrated protoxide precipitates of a very dark brown colour. This oxide is easily deprived of its water by heat, but a violent calcination is necessary to reduce it to the metallic state.

The palladous salts are for the most part brown or red; their taste is astringent, but not metallic. When ignited alone, or when gently heated in hydrogen gas, they yield metallic palladium. The metal is precipitated from the solutions of palladous salts by *phosphorus*, by *sulphurous acid*, by *nitrate of potash*, by all the *metals* which reduce silver, by *formiate of potash*, and by *alcohol* at a boiling heat. *Hydrosulphuric acid* and *hydrosulphate of ammonia* throw down the brown sulphide of palladium, insoluble in the latter reagent. *Hydriodic acid* and *iodide of potassium* throw down a black precipitate of iodide of palladium, visible even to the 500,000th degree of dilution. This reaction serves for the separation of iodine from bromine; for alkaline bromides do not precipitate palladous salts. *Potash* or *soda* forms a brown precipitate of a basic salt, soluble, with the aid of heat, in excess of the reagent. *Ammonia* produces no precipitate in a solution of palladous nitrate; but from a solution of the chloride it throws down a flesh-coloured precipitate of ammonio-chloride of palladium, soluble in excess of ammonia. The *carbonates of potash* and *soda* form a brown precipitate of hydrated palladous oxide. Carbonate of ammonia acts like ammonia. *Phosphate of soda* forms a brown precipitate. *Ferrocyanide* and *ferricyanide of potassium* form no precipitates, but the liquid after a while coagulates into a jelly. *Cyanide of mercury* throws down a white precipitate of cyanide of palladium. *Protochloride of tin* forms a black precipitate, which dissolves with intense green colour in hydrochloric acid. *Protosulphate of iron* precipitates palladium slowly from the nitrate, but not from the chloride. The reactions of palladium with hydrosulphuric acid, cyanide of mercury, and iodide of potassium taken together, serve to distinguish it from all other metals.

Protosulphide of palladium, PdS, is obtained by precipitating a palladous salt by hydrosulphuric acid, and is of a dark brown colour; it may also be prepared by the direct union of its elements.

Protochloride of palladium, PdCl, is prepared by dissolving palladium in hydrochloric acid, to which a little nitric acid is added, and evaporating the solution to dryness, to expel the excess of acid. The compound is a mass of a dark brown colour, which becomes black when made anhydrous by heat, and may be fused in a glass vessel. When heated in platinum vessels, it becomes contaminated with the protochloride of that metal. When dissolved with chloride of potassium, it forms a double salt, KCl.PdCl, which is soluble in cold, and considerably more so in hot water, and crystallizes in four-sided prisms, of a dull yellow colour. Protochloride of palladium also combines with chloride of ammonium and chloride of sodium, according to Bonsdorff, and forms double salts with most other chlorides.

Protocyanide of palladium, PdCy, is always formed when cyanide of mercury is added to a neutral solution of palladium, as a light-coloured precipitate, which becomes grey after drying. When the solution of palladium is acid, no precipitate is formed, and when the solution contains copper, the precipitate has a green colour. Palladium appears to have a greater affinity for cyanogen than any other metal. Even cyanide of mercury is decomposed when boiled with protoxide of palladium, and cyanide of palladium formed. When this cyanide is dissolved in ammonia, and the excess of the latter allowed to escape by evaporation, a precipitate of brilliant, colourless, crystalline plates is formed, which appears to consist of ammoniacal cyanide of palladium.

Nitrate of palladium, $PdO.NO_5$, is formed by dissolving the metal in nitric acid; the solution dries up into a dark red saline mass. When an excess of ammonia is added to an acid solution of this salt, and the solution evaporated by a gentle heat, a colourless nitrate of palladium and ammonium is deposited in rectangular tables.

Bioxide of palladium, Peroxide of palladium, Palladic oxide, PdO_2, 69·27 *or* 865·9.—To prepare this oxide, Berzelius recommends a solution of the hydrate or carbonate of potash to be added by small quantities at a time, to the dry bichloride of palladium and potassium, mixing well after each addition. A yellowish brown powder separates, which is the hydrated bioxide, retaining a little alkali. Washed with boiling water, it loses the greater part of its combined water, and becomes black. This oxide dissolves with difficulty in acids; the solutions are yellow. The corresponding bisulphide of palladium has not been formed.

Bichloride of palladium, $PdCl_2$, is obtained in solution, when the protochloride is dissolved in concentrated aqua-regia, and the solution only slightly heated. Its solution is of so dark a brown as to appear black, and gives a red precipitate with chloride of potassium. When the solution is diluted or heated, chlorine gas is evolved, and protochloride of palladium reproduced. The double salt of this chloride and chloride of potassium is obtained by treating the double protochloride of palladium and potassium in fine powder with aqua-regia, and evaporating the supernatant fluid to dryness. It forms a cinnabar red powder, in which little octohedral crystals can be perceived, both the palladic and palladous double chlorides being isomorphous with the corresponding compounds of platinum. When treated with hot water, this double salt emits chlorine, and is in a great measure decomposed. The salts of bioxide of palladium are scarcely known.

Ammoniacal compounds of palladium.—A moderately concentrated solution of protochloride of palladium treated with a slight excess of ammonia, yields a beautiful flesh-coloured or rose-coloured precipitate, consisting of NH_3PdCl. This precipitate dissolves in a larger excess of ammonia; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in the moist state to 212°, or in the dry state to 392°. The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. For this reason, Hugo Müller, who has lately made the ammoniacal compounds of palladium the subject of an elaborate examination, regards the red compound as *ammonio-palladous chloride,* $NH_3.PdCl$, and the yellow, as *chloride of palladammonium,* $\overbrace{NH_3Pd}\,.\,Cl$. The yellow compound, digested with water and oxide of silver, yields the *oxide of palladammonium* (or *palladamine*), $NH_3Pd.O$. This compound is a strong base, analogous to *oxide of platammonium* (p. 614). It is soluble in water, to which it communicates a strong alkaline taste and reaction; by evaporating the solution in vacuo, the base is obtained in the form of a crystalline mass, which absorbs carbonic acid rapidly from the air, especially when moist. It unites with acids, forming definite salts. Its solution precipitates the salts of silver and copper, and an excess of it does not redissolve the precipitates. *Sulphite of palladammonium,* $\overbrace{NH_3Pd}\,.\,SO_3$, is formed by saturating the solution of the oxide with sulphurous acid, or by the action of that acid on the yellow chlorine-compound: it crystallizes in orange-yellow octohedrons. The *sulphate,* $\overbrace{NH_3Pd}\,.\,SO_4$, crystallizes in a similar manner. The nitrate, iodide, and bromide have also been formed. The *fluoride* is obtained by adding the chloride to a solution of fluoride of silver.

Chloride of ammopalladammonium (or *chloride of palladdiamine,* according to Müller),

$$2NH_3\,.\,PdCl = NH_2\overbrace{(NH_4)\,Pd}\,.\,Cl,$$

separates from the ammoniacal solution of chloride of palladammonium, in colourless, oblique rhombic prisms, which at 392° give off half their ammonia and are reduced to $NH_3Pd.Cl$. The *iodide* and *bromide* of ammopalladammonium are likewise obtained by treating the solutions of iodide and bromide of palladium or palladammonium with ammonia. They both crystallize readily. The *fluoride* is obtained by adding ammonia to the solution of chloride of palladammonium in fluoride of silver, and evaporating: it forms oblique rhombic prisms. The *silico-fluoride* is obtained in crystalline scales on adding hydrofluosilicic acid to any soluble salt of ammopalladammonium. *Oxide of ammopalladammonium,* $N\overbrace{H_3Pd}.O$.—By decomposing the solution of the chloride with oxide of silver,—or better, the sulphate with hydrate of baryta, a strongly alkaline solution is obtained, which, on evaporation, leaves the hydrated oxide in the form of a crystalline mass, though not quite pure. The solution precipitates the salts of aluminium, iron, cobalt, nickel, and copper, but not those of silver; expels ammonia from chloride of ammonium, on boiling; and absorbs carbonic acid from the air. The *carbonate* obtained in this manner, or by decomposing the chloride with carbonate of silver, or the sulphate with carbonate of baryta, crystallizes in shining, colourless prisms, which turn yellow a little above 212°; the solution is strongly alkaline, and gives copious precipitates with salts of lime, baryta, copper, and silver. The *sulphite*, $N\overbrace{H_2(NH_4)Pd}.SO_3$, obtained by direct combination, or by the action of ammonia on sulphite of palladammonium, forms small prismatic crystals, sparingly soluble in water, insoluble in alcohol, and turning yellow at about 392°. The *sulphate* obtained by treating palladous sulphate with excess of ammonia, forms small colourless prisms, easily soluble in water, but insoluble in alcohol (Hugo Müller).*

ESTIMATION AND SEPARATION OF PALLADIUM.

Palladium is always estimated in the metallic state. It is precipitated from its solutions in the form of cyanide by means of a solution of cyanide of mercury, the liquid not containing any excess of acid. The precipitated cyanide of palladium is then reduced to the metallic state by calcination.

Palladium may be separated from nearly all other metals either by precipitation as cyanide, or by precipitation with hydrosulphuric acid, or by the solubility of its oxide in ammonia. But to separate it from copper, with which it is associated in platinum ore, the two metals are precipitated together by hydrosulphuric acid, and the precipitate, while still moist, roasted, together with the filter, as long as sulphurous acid continues to escape. The metals are thereby converted into basic sulphates, which must be dissolved in hydrochloric acid, the solution mixed with nitric acid and chloride of potassium, and evaporated to dryness. A dark saline mass is thus obtained, consisting of chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium; and on treating this mass with alcohol of sp. gr. 0·833, the two former salts are dissolved, and the double chloride of palladium and potassium remains.

SECTION III.

IRIDIUM.

Eq. 98·68 *or* 1233·5; Ir.

The black scales which remain when native platinum is dissolved in aqua-regia, were discovered by Mr. Smithson Tennant to contain iridium and osmium.† The

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* Ann. Ch. Pharm. lxxxvi. 341.

† Phil. Trans. 1804.

same alloy occurs in flat white metallic grains in native platinum. Iridium has also been observed in combination with about 20 per cent. of platinum, crystallized in octohedrons, which are whiter than platinum, and are said to have a greater density, namely 22·66.

The separation of the osmium and iridium is effected by the following methods: —1. The osmide of iridium is mixed with an equal weight of common salt, and subjected to the action of a stream of chlorine in a porcelain tube heated to redness. Double chlorides of iridium and sodium, and of osmium and sodium, are then formed; and if the chlorine is moist, a certain quantity of osmic acid, which volatilizes, and may be condensed in aqueous ammonia. The mixture of the double chlorides is detached from the tube and boiled with nitric acid. Osmic acid is then evolved, and may be condensed in an alkaline solution, while the chloride of sodium and iridium remains in the solution, and, when mixed with sal-ammoniac, yields a precipitate of chloride of iridium and ammonium, which, on ignition, leaves pure metallic iridium (Wöhler).—2. A mixture of 100 grammes of osmide of iridium and 300 grammes of nitre is placed in an earthen crucible, and heated to bright redness for an hour, the resulting mixture of osmiate and iridiate of potash poured out on a cold metal plate, then introduced into a tubulated retort, and distilled with a large excess of nitric acid. A large quantity of osmic acid then volatilizes and condenses in the receiver in beautiful white crystals. As soon as the evolution of osmic acid ceases, water is added, and the residue, consisting of oxide of iridium, with a certain quantity of oxide of osmium, is collected on a filter and boiled with aqua-regia, which dissolves the two metals as chlorides. The solution is then mixed with sal-ammoniac, which precipitates chloride of osmium and ammonium, and bichloride of iridium and ammonium; and the mixed precipitate suspended in water and exposed to a current of sulphurous acid, whereby the compound $IrCl_2 . NH_4Cl$, is converted into $IrCl . NH_4Cl$, which dissolves, while the chloride of osmium and ammonium remains unaltered and does not dissolve: this latter chloride yields pure metallic osmium by calcination. The solution of protochloride of iridium and ammonium leaves, when evaporated, beautiful brown crystals, which yield metallic iridium by calcination.

Iridium is obtained immediately from the chloride, by decomposing that salt with hydrogen at a gentle heat, or by exposing it alone to a very high temperature, in the form of a grey metallic powder, much resembling spongy platinum; also, as above described, from the chloride of iridium and ammonium. It is one of the most refractory bodies known, not being fused by the oxyhydrogen blowpipe. Mr. Children, however, succeeded in fusing a portion of iridium into a globule, by the discharge of a very large voltaic battery. This globule was white and very brilliant, but still a little porous; its density was 18·68. Iridium is neither ductile nor malleable; but it may be obtained in the form of a compact mass, very hard, and capable of taking a good polish, by moistening the pulverulent metal with a small quantity of water, compressing it lightly at first with filtering paper, afterwards very forcibly in a press, and calcining it at a strong white heat in a forge fire. The metal thus aggregated is very porous, and its density does not exceed 16·0. Iridium becomes white and brilliant by strong ignition, without fusion, and is afterwards insoluble in acids. If reduced by hydrogen at a low temperature, it oxidates slowly when heated to redness, or when digested in aqua-regia. This metal is generally rendered soluble by one or other of the following operations. It is calcined with hydrate of potash or nitre, or with a mixture of these salts, which gives a compound of sesquioxide of iridium and potassium. Or, the metal is reduced to a fine powder, and intimately mixed with an equal weight of chloride of potassium or sodium, and the mixture heated to low redness in a stream of chlorine gas. The metal then combines with chlorine, and the double chloride of iridium and potassium or sodium is formed, which is soluble in water.

Oxides of iridium. — Iridium forms four compounds with oxygen, which are obtained by decomposing the corresponding chlorides. The *protoxide of iridium*, IrO, is obtained from the chloride produced when iridium is heated in chlorine gas; also by precipitating the double chloride of iridium and potassium (KCl.IrCl) with carbonate of potash. The hydrate is then obtained of a greenish grey colour, which is soluble in an excess of the alkaline carbonate. This oxide is the base of a class of salts. The *sesquioxide of iridium*, Ir_2O_3, is formed when the metal is calcined with hydrate of potash or nitre. Berzelius recommends as the best process for procuring it, to mix the double bichloride of iridium and potassium ($KCl + IrCl_2$) with twice its weight of carbonate of potash, and expose it to a low red heat. On dissolving out the alkaline salt, the sesquioxide remains as a very fine powder, of a black colour with a shade of blue. A heat above the melting point of silver is required to expel the oxygen from this oxide. It is reduced to the metallic state by hydrogen gas at the usual temperature, an effect which appears to arise from the oxide of iridium having the property, as well as the metal, to determine the oxidation of hydrogen, a reaction which causes the oxide to be heated to the temperature at which it is itself reduced by hydrogen. The hydrate of this oxide dissolves in acids and forms a particular class of salts, the solutions of which are sometimes of a very dark colour, resembling a mixture of water and venous blood.

Binoxide of iridium, or Iridic oxide, IrO_2. — A solution of sesquichloride of iridium mixed with potash yields no precipitate at first; but if the liquid be heated out of contact with the air, it quickly assumes an indigo colour, absorbs oxygen from the air, and deposits hydrated iridic oxide, $IrO_2.2HO$, which may be rendered anhydrous by calcination. This oxide is likewise obtained by dissolving the hydrated sesquioxide in potash, and treating the solution with an acid. A greenish-blue precipitate is then formed, which gradually absorbs oxygen from the air, and assumes an indigo colour (Claus). This oxide forms salts whose solutions are of a dark, brown-red colour and almost opaque when concentrated, but reddish-yellow when dilute. *Hydrosulphuric acid* decolorizes the solutions at first, and afterwards forms a brown precipitate; *hydrosulphate of ammonia* also forms a brown precipitate. *Potash* and *ammonia* decolourize the solution, and produce only a slight black precipitate; but the liquid, on exposure to the air, soon acquires a very fine blue colour. *Carbonate of potash* forms a red-brown precipitate, which gradually dissolves, the liquid afterwards turning blue when exposed to the air. *Carbonate of ammonia* imparts a blue colour to the liquid under the influence of the air. *Chloride of ammonium* forms a dark, cherry-red pulverulent precipitate of bichloride of iridium and ammonium. *Ferrocyanide of potassium* and *protosulphate of iron* decolourize the solution. *Protochloride of tin* forms a light brown precipitate. *Zinc* precipitates metallic iridium as a black powder.

Teroxide of iridium, IrO_3, is formed in small quantity when the alloy of osmium and iridium fused in nitre is digested in aqua-regia. The double terchloride of iridium and potassium then formed yields a rose-red solution, which, when treated with an alkali, slowly deposits the teroxide as a greenish-yellow precipitate, retaining, however, a certain quantity of the alkali. The salts of the protoxide and teroxide afford blue and purple solutions when mixed, depending probably on the formation of one or more combinations of these oxides. The name iridium (from Iris) was applied to this metal, from the variety of colours which its preparations exhibit.

Sulphides of iridium, corresponding with the oxides of the same metal, have been formed.

Chlorides of iridium. — The *protochloride*, IrCl, is formed when iridium in powder is heated to low redness in chlorine gas. As thus prepared, it is insoluble in water, but slightly soluble in hydrochloric acid. It forms double salts with the chlorides of potassium, ammonium, and sodium.

The *sesquichloride*, Ir_2Cl_3, is prepared by dissolving the sesquioxide in hydrochloric acid. It is black, deliquescent, and does not crystallize. It forms soluble double chlorides, which are decomposed by ebullition into iridous double chlorides (containing $IrCl$), which remain in solution, and iridic double chlorides (containing $IrCl_2$), which are precipitated. Claus has obtained the compounds, $3KCl . Ir_2Cl_3 + 6HO$; $3NH_4Cl . Ir_2Cl_3 + 3HO$; and $3NaCl . Ir_2Cl_3 + 24HO$.

The *bichloride*, $IrCl_2$, is obtained by dissolving very finely-divided iridium, or one of its oxides, in aqua-regia, the liquid being heated to the boiling point. It dissolves in water, forming a reddish-yellow solution. It combines with other chlorides, forming very definite salts. The potassium-salt, *chloridiate of potassium*, $IrCl_2 . KCl . HO$, crystallizes in black octohedrons, yielding a red powder, and soluble in water, to which it imparts a red colour. *Chloridiate of ammonium*, $IrCl_2 . NH_4Cl . HO$, is obtained, on mixing the solutions of the two chlorides, as a very dark brown precipitate, which dissolves in boiling water, and crystallizes in octohedrons on cooling. Its colouring power is very great, 1 part of it sufficing to impart a distinct coloration to 40,000 parts of water. The red colour often exhibited by chloroplatinate of ammonium is due to traces of this salt. Chloridiate of ammonium dissolves in sulphurous acid, and is thereby converted into a soluble and crystallizable compound of NH_4Cl, and $IrCl$; the separation of iridium and osmium depends upon this property. Bichloride of iridium, free or combined with other chlorides, is also reduced to the state of protochloride by potash, hydrosulphuric acid, ferrocyanide of potassium, and alcohol. According to Claus,* the bichloride is converted by potash into the olive-green sesquichloride, hypochlorite of potash being formed at the same time. The alkaline solution when heated becomes colourless, and afterwards violet-red, and yields a blue precipitate of the hydrated bioxide; the decolourized alkaline solution, mixed with a few drops of alcohol and heated, deposits metallic iridium. Nitrate of silver added to the solution of the bichloride forms a blue precipitate, which quickly loses its colour and passes into the compound $Ir_2Cl_3 . 3AgCl$. Mercurous nitrate forms a light ochre-yellow precipitate of $Ir_2Cl_3 . 3Hg_2Cl$.

Terchloride of iridium, $IrCl_3$, is formed by treating an oxide or a lower chloride of iridium with very strong aqua-regia, at a temperature not exceeding 104° or 122° (40° or 50° C.) Its colour is a deep brown, nearly approaching to black; it is soluble in water, and deliquescent. It forms double chlorides of the alkali-metals.

Carburet of iridium.—When a coherent mass of iridium is held in the flame of a spirit lamp, black masses appear on its surface, which are a carburet, containing 19·83 per cent. of carbon, or IrC_4. The carbon burns off readily in the air.

Iridic sulphate is obtained by dissolving bisulphide of iridium in nitric acid, and expelling the excess of acid by evaporation. It dissolves in water and alcohol, forming orange-yellow solutions, which on evaporation leave the salt in the form of a syrupy uncrystallizable mass.

AMMONIACAL COMPOUNDS OF IRIDIUM.—*Ammonio-iridious chloride*, $NH_3 . IrCl$, or *Chloride of iridammonium*, $\overbrace{NH_3Ir} . Cl$.—Prepared by heating bichloride of iridium till it is converted into protochloride, dissolving the brown resinous residue in carbonate of ammonia, and adding hydrochloric acid in slight excess. The compound then separates in the form of a yellow granular precipitate, insoluble in water. The oxide corresponding to this chloride has not been obtained in the free state. The *sulphate* $\overbrace{NH_3Ir} . SO_4$ is obtained by heating the chloride with dilute sulphuric acid. It crystallizes in large orange-yellow laminæ, easily soluble in water. *Biammonio-iridious chloride*, $2NH_3 . IrCl$, or *Chloride of ammiridammonium*, $NH_2\overbrace{(NH_4)Ir} . Cl$, is obtained, as a white precipitate, by boiling the compound, $NH_3Ir . Cl$, with excess of ammonia. Treated with moderately strong sulphuric acid, it yields the corresponding sulphate, $NH_2\overbrace{(NH_4)Ir} . SO_4$,

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* Liebig and Kopp's Jährbericht, 1855, p. 427.

in rhombic prisms; and, by decomposing this salt with nitrate of baryta, or decomposing the chloride with nitric acid, the nitrate is obtained in yellow needles, which dissolve readily in water, melt when heated, and then suddenly decompose with flame. A *chloronitrate of ammiridammonium*, $\mathrm{N\overbrace{H_2(NH_4)}Ir}\,.\left\{\begin{matrix}\mathrm{NO_6}\\ \mathrm{Cl}\end{matrix}\right.$, or *nitrate of ammochloriridammonium*, $\mathrm{N\overbrace{H_2(NH_4)\,(IrCl)}\,.\,NO_6}$, analogous to Gros's platinum-nitrate (p. 616), is obtained as a yellowish, crystalline, granular mass, by heating the chloride of iridammonium, $\mathrm{NH_3Ir\,.\,Cl}$, with strong nitric acid; when recrystallized from water, it forms shining yellow, laminar crystals. *Bichloride of ammiridammonium*, $\mathrm{NH_2\overbrace{(NH_4)}Ir\,.\,Cl_2}$, or *chloride of ammo-chloriridammonium*, $\mathrm{N\overbrace{H_2(NH_4)(IrCl)}\,.\,Cl}$, is obtained by treating the last-mentioned salt with hydrochloric acid, in the form of a violet precipitate, which dissolves readily in hot water, and separates from the solution in violet crystals. Nitrate of silver added to the solution throws down only half the chlorine. The nitrate, treated with dilute sulphuric acid, yields the chlorosulphate of ammiridammonium in delicate greenish, needle-shaped crystals (Skoblikoff).

The compound $\mathrm{5NH_3\,.\,IrCl_3}$, or $\left.\begin{matrix}\mathrm{NH_2\overbrace{(NH_4)Ir}}\\ \mathrm{NH\overbrace{(NH_4)_2}Ir}\end{matrix}\right\}\mathrm{Cl_3}$, is obtained by mixing a dilute solution of $\mathrm{Ir_2Cl_3 + 3NH_4Cl}$, mixed with excess of ammonia, and leaving the mixture in a well-closed and completely filled bottle for some weeks in a warm place; heating the liquid, which has then acquired a rose-colour, to expel the excess of ammonia; neutralizing with hydrochloric acid; evaporating to dryness; and treating the greenish yellow residue with cold water to extract the chloride of ammonium. A light flesh-coloured, finely crystalline powder then remains, which, when dissolved in boiling water, acidulated with hydrochloric acid, yields, on cooling, a crystalline precipitate of $\mathrm{5NH_3\,.\,Ir_2Cl_3}$ mixed with sesquichloride of iridium. This compound when dissolved in a boiling solution of ammonia, is partially decomposed, with separation of blue hydrated bioxide of iridium; when digested with water and oxide of silver, it yields a rose-coloured alkaline solution of the base $\mathrm{5NH_3\,.\,Ir_2O_3}$. This solution, saturated with various acids, yields:— the *carbonate* $\mathrm{5NH_3\,.\,Ir_2O_3\,.\,3CO_2 + 3HO}$, in the form of a finely crystalline powder, having a light flesh-coloured and alkaline reaction; the *nitrate*, $\mathrm{5NH_3.Ir_2O_3.3NO_5}$, in indistinct, light flesh-coloured, neutral prisms; and the *sulphate*, $\mathrm{5NH_3\,.\,Ir_2O_3\,.\,2SO_4}$, as a neutral crystalline salt of similar colour. All these salts are soluble in water (Claus).

ESTIMATION AND SEPARATION OF IRIDIUM.

The quantitative estimation of iridium is effected in the same manner as that of platinum, viz., by precipitating with sal-ammoniac and igniting the precipitate. The same method serves to separate iridium from all the preceding metals except platinum. The separation of these two metals is effected by the method already described for the preparation of pure platinum (p. 610); viz., by precipitating with chloride of potassium, fusing the precipitate with carbonate of potash, and dissolving out the platinum with aqua-regia.

SECTION IV.

OSMIUM.

Eq. 99·56 *or* 1244·5; Os.

In the treatment of the alloy of iridium and osmium, the latter is separated as a volatile oxide, or osmic acid (p. 624). To obtain the metal, a solution of osmic acid is mixed with hydrochloric acid, and digested with mercury in a well closed bottle at a temperature of 104° (40° Cent.). The osmium is reduced by the mercury, and an amalgam formed, which is distilled in a retort, through which a stream of hydrogen is passed, till all the mercury and calomel formed are removed: osmium then remains as a black powder without metallic lustre. Metallic osmium is also obtained by igniting the sesquichloride of osmium and ammonium mixed with sal-ammoniac.

When rendered coherent, osmium is a white metal, less brilliant than platinum, and very easily pulverized. Its density is about 10. As obtained from the amalgam, osmium is highly combustible; when a mass of it is ignited at a point, it continues to redden, and burns without residue, being converted into the volatile oxide or osmic acid. Osmium in the same condition is oxidated by nitric acid or aqua-regia, and the osmic acid formed distils over with the water and acid. But after being exposed to a red heat, osmium becomes much less combustible in air, and is not oxidated by the humid way, resembling silicon and titanium in that respect. Six different oxides of this metal have been obtained, namely, OsO; Os_2O_3; OsO_2; OsO_3; OsO_4; and OsO_5. The three lowest of these oxides are analogous in composition to the oxides of iridium.

Chlorides and oxides of osmium.—When osmium is heated in a long glass tube by a spirit lamp, and chlorine gas passed over it, two chlorides are formed, which condense separately in the tube, owing to a difference in their volatility. The *protochloride*, $OsCl$, which is the least volatile, crystallizes in needles of a deep green colour. It is deliquescent, and forms a green solution remarkable for its beauty. This solution is instantly discoloured by great dilution, metallic osmium being deposited, and hydrochloric and osmic acids remaining in solution. Chloride of osmium combines with alkaline chlorides, and acquires greater stability. The *protoxide*, OsO, is obtained by adding potash to a solution of protochloride of osmium and potassium; after some hours, a deep green, almost black, powder is precipitated, which is the hydrated oxide. This hydrate contains alkali. It dissolves slowly but completely in acids, and gives solutions of a deep green colour.

Sesquioxide of osmium, Os_2O_3, is not known in the separate state; but when a mixture of osmic acid and ammonia is kept for some hours at a temperature of 100° to 120°, nitrogen gas is evolved, and a black substance is deposited, containing the sesquioxide in combination with ammonia. It dissolves slowly in acids, and forms yellowish brown solutions, which become brown-black when they contain much oxide. The metal is not precipitated from these solutions by zinc or iron. The corresponding *sesquichloride of osmium* is obtained in combination with chloride of potassium as a double salt, when the preceding oxide containing ammonia is dissolved in hydrochloric acid, and evaporated to dryness; the compound is not crystalline.

Bichloride of osmium, $OsCl_2$, is the more volatile chloride produced when osmium is heated in chlorine. It condenses as a dark red floury powder. Exposed to air, it attracts a little moisture, and forms dendritic crystals. It is soluble in a small quantity of water, giving a yellow solution, but is decomposed by a large quantity, like the protochloride. The bichloride of osmium and potassium is prepared in the same manner as the corresponding salt of iridium. In powder, it is of a red colour like minium, but forms also the usual octohedral crystals, $KCl.OsCl_2$, which are brown. A solution of this double salt, mixed with carbonate of potash or soda, affords after a time, or immediately, if heated, the corresponding *bioxide of osmium* or *osmic oxide*, OsO_2, as a brown powder, which appears black when collected. This oxide, like the peroxide of iridium, is reduced by hydrogen at ordinary temperatures. It is a base capable of uniting with acids at the moment of its formation.

Osmic sulphate is obtained by treating one of the sulphides of osmium with nitric acid; when dried as completely as possible, it forms a dark yellowish brown syrup, which dissolves in water. The reaction of osmic salts (*e. g.* of the bichloride of osmium and potassium) in solution, are as follows:—*Potash* forms a black precipitate, slowly in the cold, immediately on boiling; *ammonia*, a brown precipitate, after some time; *carbonate of potash*, the same; *chloride of ammonium*, a red precipitate; *protochloride of tin*, a brown precipitate; *mercurous nitrate*, yellowish white; *nitrate of silver*, dark olive-green; *hydrosulphuric acid*, a yellowish brown precipitate after some time; *hydrosulphate of ammonia*, a yellowish brown precipitate insoluble in excess. No precipitate is formed by oxalic acid, ferrocyanide or ferricyanide of potassium, or ferrous sulphate. *Zinc* throws down part of the osmium in the metallic state. *Iodide of potassium* does not form any precipitate, but imparts a deep purple-red colour, which does not disappear when the liquid is heated. *Tannic acid* imparts a deep blue colour.

Osmious acid, OsO_3.—This acid is not known in the separate state, being resolved at the moment of separation from its combinations, into osmic acid and osmic oxide, $2OsO_3 = OsO_4 + OsO_2$. *Osmite of potash*, $KO.OsO_3 + 2HO$, is obtained by the action of reducing agents on the osmiate; thus, when a few drops of alcohol are added to a solution of osmiate of potash, the osmite is precipitated in the form of a rose-coloured crystalline powder, a strong odour of aldehyde being at the same time evolved, due to the oxidation of the alcohol. Osmite of potash may be obtained in octohedral crystals of considerable size, by mixing a solution of osmiate with nitrite of potash, and leaving the mixture to evaporate slowly. The salt is likewise obtained by dissolving osmic oxide in osmiate of potash. It is rose-coloured, soluble in water, insoluble in alcohol and ether, permanent in dry air, but changes into osmiate under the influence of air and water. Chlorine converts it into osmic oxide and osmiate of potash. It is decomposed by acids, even by the weakest, osmic oxide being precipitated and osmic acid evolved. Sulphurous acid introduced into a solution of this salt, previously rendered alkaline, throws down a yellow crystalline precipitate, containing a salt whose acid is formed of osmium, oxygen, and sulphur. Chloride of ammonium decomposes osmite of potash, forming a nearly insoluble yellow salt, $NH_4Cl.OSO_2NH_2$, which may be regarded as a compound of sal-ammoniac with *osmiamide*, OsO_2NH_2. This compound, heated in a stream of hydrogen, gives off ammonia and sal-ammoniac, and leaves metallic osmium. *Osmite of soda* is prepared in the same manner as osmite of potash, but does not crystallize so easily; its solutions are rose-coloured. Osmious acid does not combine with ammonia; the osmites of potash and soda are rapidly reduced by ammonia.

A *terchloride of osmium* has been obtained in combination with chloride of ammonium, as a double salt, when osmic acid is saturated with ammonia, and treated after a while with excess of hydrochloric acid, mercury being also placed in contact with it. After a few days, the liquid loses the odour of osmic acid, and when evaporated to dryness, leaves the double salt in brown dendritic crystals.

Osmic acid, OsO_4, or the volatile oxide of osmium, is best obtained by the combustion of osmium in a glass tube through which a stream of oxygen gas is passed; it is also obtained by the action of nitric acid on osmium, and in the decomposition of osmites or osmates by acids. It condenses in long, colourless, regular prismatic needles. The odour of this compound is extremely acid and penetrating, resembling that of the chloride of sulphur. It was from this property of its acid, which is so constantly observed when the oxidable compounds of osmium are heated in air, that osmium obtained its name (from ὀσμος, odour). Its taste is acrid and burning, but not acid. It becomes soft like wax by the heat of the hand, melts into a colourless liquid like water, considerably below 212°, and enters into ebullition a very little above its point of fusion. It is dissolved slowly, but in considerable quantity, by water. The solution has no acid reaction. Osmic acid is also soluble in alcohol and ether, but these solutions are apt to deposit metallic osmium. It is a weak acid, being incapable of displacing carbonic acid from the carbonates, in the humid way, but forms a class of salts, the osmiates. Osmic acid is expelled by heat from most of its combinations with bases.

An acid containing more oxygen than osmic acid, and apparently having the formula OsO_5, is formed by submitting the osmiates to the action of oxygen and oxidizing agents. It is very unstable; its potash and soda-salts have a dark brown colour, and sometimes crystallize in the alkaline liquids. If the formula OsO_5 be correct, the oxidation-series of osmium will present remarkable analogies with those of nitrogen, phosphorus, and arsenic (Fremy).

Osmiamic acid, Os_2NO_5.—Formed by the action of ammonia on osmic acid, $2OsO_4 + NH_3 . Os_2NO_5O + 3HO$. Its potash-salt is obtained by adding ammonia to a hot solution of osmic acid in excess of potash; the deep orange colour of the liquid soon changes to light yellow, and osmiamate of potash separates in the form of a yellow crystalline powder. The osmiamates of the alkalies and alkaline earths and the zinc-salt are soluble in water; the lead, mercury, and silver-salts insoluble. The aqueous acid is obtained by decomposing the baryta-salt with sulphuric, or the silver-salt with hydrochloric acid. It may be kept for some days when dilute, but soon decomposes in the concentrated state. It is a powerful acid, decomposing not only the carbonates, but even chloride of potassium. Fritzsche and Struve,* who discovered this acid, assign to it the formula Os_2NO_4, regarding it as a compound of nitride of osmium with osmic acid; $OsN.OsO_4$. Gerhardt, on the contrary,† assigns to it the formula above given, viz., Os_2NO_5, which is the more probable of the two, inasmuch as, if Fritzsche and Struve's were correct, the formation of the acid must be attended with the evolution of 1 eq. oxygen; but they particularly observe that no escape of gas takes place.

Sulphides of osmium.—Osmium has a great affinity for sulphur, and burns in its vapour. Five sulphides of osmium are known, corresponding to all the oxides except the highest, viz., OsS, Os_2S_3, OsS_2, OsS_3, OsS_4. The first four of these sulphides are obtained by decomposing the corresponding chlorides with hydrosulphuric acid. The tetrasulphide is prepared by passing hydrosulphuric acid gas into a solution of osmic acid: it is a sulphur-acid, completely insoluble in water; whereas the others are sulphur bases, slightly soluble in water, and forming deep yellow solutions.

ESTIMATION AND SEPARATION OF OSMIUM.

Osmium is generally estimated in the metallic state. The best mode of separating it from the metals with which it is usually accompanied, is to volatilize it in the form of osmic acid—by distillation with aqua-regia, if the compound be perfectly soluble therein, or by roasting in a stream of oxygen—receiving the vapours of osmic acid in a strong solution of potash; and to reduce this salt, by the addition of a few drops of alcohol, to osmiate of potash, which is insoluble in the alcoholic liquor. The osmite of potash is then digested in a cold solution of sal-ammoniac, whereby the compound $NH_4Cl . OsO_2NH_2$ is produced, and the osmium reduced to the metallic state by igniting this last-mentioned compound in a current of hydrogen gas (Fremy).

Another mode of proceeding is to condense the acid vapours evolved by distilling a compound of osmium with aqua-regia in a well-cooled receiver, and pre-

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* J. pr. Chem. xli. 97.

† Compt. rend. de Trans. en Chimie. 1847, 304

cipitate the osmium from the solution by metallic mercury. A precipitate is thereby obtained consisting of calomel, a pulverulent amalgam of osmium, and metallic mercury containing a very small quantity of osmium. This mixture is heated in a glass bulb, through which a stream of hydrogen is passed, whereupon the mercury and its chloride volatilize, and metallic osmium is left in the form of a black powder. The liquid, however, still retains a small quantity of osmium, which may be isolated by saturating the liquid with ammonia, evaporating to dryness, and calcining the residue (Berzelius). The osmium may also be precipitated from the distilled liquid by hydrosulphuric acid, the solution, after complete saturation, being left for several days in a stoppered bottle, till the sulphide of osmium is completely deposited. The sulphide is then washed, dried, and weighed; but as it is apt to retain moisture, and, moreover, oxidizes to a certain extent in the air, the method is not very exact. It is recommended, however, for the estimation of small quantities of osmium, the method of precipitating by mercury being better adapted for larger quantities (Berzelius).

SECTION V.

RHODIUM.

Eq. 52 *or* 651·4; R.

This metal was discovered, by Wollaston, in the ore of platinum He found the ore from Brazil to contain 0·4 per cent.; native platinum from another locality has been found with as much as 3 per cent. of rhodium.

After the precipitation of the palladium from the solution of native platinum, by cyanide of mercury, the solution, in order to obtain the rhodium, may be mixed with carbonate of soda and excess of hydrochloric acid, and evaporated to dryness. The cyanide of mercury in excess is decomposed by the hydrochloric acid, and converted into chloride of mercury. The dried mass is reduced to a very fine powder, and washed with alcohol of density 0·837, which takes up the double chlorides of sodium with platinum and iridium, the copper and the mercury, but leaves the double chloride of rhodium and sodium in the form of a fine deep red powder. The rhodium is most easily reduced by gently heating the double chloride in a stream of hydrogen gas, and afterwards washing out the chloride of sodium by water.

Rhodium, when rendered coherent, is a white metal like platinum; its density is about 10·6. It is brittle and very hard, and may be reduced to powder. When pure, it is not dissolved by any acid; but when alloyed with certain metals, such as platinum, copper, bismuth, or lead, and exposed to aqua-regia, it dissolves along with those metals. When fused with gold or silver, however, it is not dissolved with the other metal. But the most eligible mode of rendering rhodium soluble, is to mix it in fine powder with chloride of potassium or sodium, and to heat the mixture to low redness in a stream of chlorine gas. A double chloride is then formed, as with the other platinum metals in similar circumstances, which is very soluble in water. The solutions of rhodium have a beautiful red colour, the circumstance from which the metal derives its name (from ῥὸδον, a rose). Rhodium may also be rendered soluble in the dry way, by fusing it with bisulphate of potash, when the metal is oxidated with escape of sulphurous acid gas. Rhodium is the most oxidable of the platinum metals, combining with oxygen when heated to redness in an open vessel, and very readily when in fine powder and heated to a cherry-red heat. It appears to form two oxides, the rhodous and the rhodic, of which, however, the last only has been completely isolated.

Oxides of rhodium.—The *protoxide* or *rhodous oxide*, RO, is formed when rhodium is ignited in contact with the air. One hundred parts of rhodium thus treated quickly increase to 115·3 parts, corresponding to the protoxide; then slowly, if the ignition be continued, to 118·07 parts; a black powder being formed, consisting of $3RO . R_2O_3$ (Berzelius).

Rhodic oxide, R_2O_3, is produced when the metal is ignited with hydrate of potash and a little nitre, in a silver crucible. The metal swells up, assumes a coffee-brown colour, and is converted into a compound of rhodic oxide and potash, which must be washed with water, and afterwards digested in hydrochloric acid; the hydrated oxide remains of a grey colour, with a shade of green, and insoluble in acids. The same hydrated oxide, as obtained from the double chloride of rhodium and potassium, or sodium, by precipitation with an alkali and evaporation, dissolves slowly in acids, together with a certain quantity of alkali which is attached to it, assuming a yellow colour, and producing double salts. The solution in hydrochloric acid is also pale, although it contains chloride of potassium, while a solution of the double chloride, prepared in the way formerly mentioned, has a fine red colour. Hence Berzelius infers that there are two isomeric modifications of this oxide, whose compounds, when in solution, are respectively yellow and rose-coloured. Hydrated rhodic oxide contains one atom of water, $R_2O_3 . HO$. Two compounds of rhodic oxide with the protoxide of the same metal appear to exist: $R_2O_3 . 3RO$, and $R_2O_3 . 2RO$. The known compounds of rhodium are not isomorphous with compounds of platinum; but this may arise from these two metals affecting combination in different proportions, so that their compounds are not analagous in composition. Their association and resemblance in other respects afford a strong presumption of their being isomorphous bodies.

Solutions of rhodic salts yield, with *hydrosulphuric acid*, a brown precipitate of protosulphide, which is slowly deposited; with *hydrosulphate of ammonia* a brown precipitate, insoluble in excess; with *sulphurous acid* and *sulphites*, a pale yellow precipitate; with *potash*, a yellow precipitate of hydrated rhodic oxide, soluble in excess; with *ammonia*, a yellow precipitate of rhodate of ammonia, which, however, does not form immediately; with *alkaline carbonates*, a yellow precipitate after a while. *Iodide of potassium* produces a slight yellow precipitate; *protochloride of tin* imparts a dark colour to the solutions, but forms no precipitate. Acetate of *lead*, *mercurous* nitrate, and nitrate of *silver* form precipitates analogous in composition to the iridium-salts already mentioned (p. 625). *Zinc* precipitates metallic rhodium. In a solution of rhodium mixed with excess of potash, *alcohol* forms, even at ordinary temperatures, a black precipitate, probably consisting of metallic rhodium; with the other platinum-metals, this reaction takes place only when the liquid is heated. No precipitate is formed by phosphate of soda, sal-ammoniac, chloride of potassium, chromate of potash, oxalic acid, cyanide of potassium, cyanide of mercury, ferrocyanide or ferricyanide of potassium, or gallic acid. *Hydrogen gas* reduces the anhydrous salts at a moderate heat.

Sulphide of rhodium. — Rhodium may be united with sulphur by either the dry or the humid way. The sulphide of rhodium was used by Wollaston to obtain the metal in a coherent mass.

Protochloride of rhodium, RCl, is obtained by heating the protosulphate (precipitated from rhodic salts by hydrosulphuric acid) in a stream of chlorine; or by digesting one of the intermediate oxides with hydrochloric acid, whereupon the sesquichloride dissolves, and the protochloride remains in the form of a reddish grey powder, insoluble in water.

Sesquichloride of rhodium, R_2Cl_3, is obtained from the double chloride of rhodium and potassium, by precipitating the latter metal with fluosilicic acid. The dry salt thus obtained is brown black, and not crystalline; it requires a pretty high temperature to decompose it, and then resolves itself at once into chlorine and rhodium. This salt deliquesces in air; its solution in water is of a beautiful red colour (Berzelius). Sesquichloride of rhodium is also obtained in the form of a rose-red powder by heating the metal to low redness in a stream of chlorine (Claus). This red powder, which was regarded by Berzelius as $R_2Cl_3 . 2RCl$, is slowly decomposed when heated in hydrogen gas, is insoluble in strong hydrochloric and aqua-regia even at the boiling heat, is coloured yellow by continued boiling with potash, and if afterwards boiled with strong hydrochloric acid, dissolves in small quantity, forming a rose-coloured solution, the greater part, however, remaining unaltered.

A *chloride of rhodium and potassium*, containing $2KCl.R_2Cl_3 + 2HO$, is obtained by the action of chlorine on a mixture of rhodium and chloride of potassium, or by evaporating a solution of the sesquichloride of rhodium and sodium with chloride of potassium. It forms brown, doubly oblique prisms, which dissolve sparingly in water. Another double salt, containing $3KCl.R_2Cl_3 + 6HO$, is obtained in dark red, sparingly soluble, efflorescent prisms, by spontaneous evaporation of a solution of the hydrated sesquioxide in hydrochloric acid mixed with chloride of potassium. The *sodium double-salt*, $3NaCl.R_2Cl_3 + 24HO$, forms doubly oblique prisms of a deep cherry-red colour. With *chloride of ammonium*, two double salts are obtained, viz., $2NH_4Cl.R_2Cl_3 + 2HO$, and $3NH_4Cl.R_2Cl_3 + 3HO$, both of which form red prismatic crystals. By precipitating either of the above double chlorides containing 2 or 3 eq. of the basic chloride to 1 eq. R_2Cl_3, with acetate of *lead*, *mercurous* nitrate, or nitrate of *silver*, rose-coloured precipitates are formed, containing 2 or 3 eq. of $PbCl$, Hg_2Cl, or $AgCl$, to 1 eq. of R_2Cl_3 (Claus).

A *sulphate of rhodium* is formed when rhodium is ignited with bisulphate of potash; it gives a yellow solution. Another sulphate in combination with sulphate of potash gradually falls as a white powder, when sulphuric acid is added to a solution of the double chloride of these bases. It is nearly insoluble in water; its formula is $KO.SO_3 + {}_2O_3.3SO_3$. *Nitrate of rhodium* is formed by dissolving the oxide in nitric acid. It forms a deliquescent salt of a dark red colour, $R_2O_3.3NO_5$; the last salt combines with nitrate of soda, forming dark red crystals soluble in water but not in alcohol: $NaO.NO_5 + R_2O_3.3NO_5$.

The salts of rhodium are often mixed with peculiar rose-coloured salts, whose nature is not exactly known. These new salts are not precipitated, either by iodide of potassium in the cold, or by sulphurous acid, or by ammonia; they form, with chloride of ammonium, double salts, which crystallize, not in scales, but in red prisms (Fremy).

ESTIMATION AND SEPARATION OF RHODIUM.

Rhodium is estimated in the metallic state. The solution containing it is mixed with excess of carbonate of soda and evaporated to dryness, the residue ignited, and the calcined mass treated with cold water: oxide of rhodium then remains, and may be reduced by hydrogen.

Rhodium is separated from many metals with which it may be alloyed, by fusing the alloy with bisulphate of potash; the rhodium is thereby converted into sulphate of rhodium and potassium, which may be dissolved out by water. The method of separating it from platinum and the allied metals has already been given.

The separation of rhodium from other metals in solution is somewhat difficult, because it is not completely precipitated by hydrosulphuric acid. To separate rhodium from *copper*, the solution is saturated with hydrosulphuric acid and left to stand in a stoppered bottle for twelve hours, then filtered, and the filtrate heated to separate an additional portion of sulphide of rhodium. The whole of the precipitate is then roasted in a platinum crucible till the sulphides are completely oxidized, and the product treated with strong hydrochloric acid, which dissolves the copper and leaves the oxide of rhodium. The liquid filtered from the hydrosulphuric acid precipitate still contains a small portion of rhodium, which may be precipitated by carbonate of soda and converted into oxide as above. The whole of the oxide is then reduced by hydrogen.

To separate rhodium from *iron*, the rhodium is precipitated as completely as possible by hydrosulphuric acid; the liquid filtered; and the iron in the filtrate precipitated by ammonia, after having been brought to the state of sesquioxide. The iron-precipitate carries down with it a certain portion of rhodium, which may be separated by igniting the precipitate in a current of hydrogen, and treating the reduced metals with hydrochloric acid, which dissolves the iron and leaves the rhodium: the latter is then converted into oxide by ignition in the air. The precipitated sulphide of rhodium is likewise oxidized by roasting. The small quantity of rhodium which remains in solution after precipitation by ammonia is precipitated by carbonate of soda, and converted into oxide by ignition. The whole of the oxide of rhodium is then reduced to the metallic state by hydrogen.

The separation of rhodium from the alkali-metals is easily effected by converting the metals into chlorides, and igniting the chlorides in a current of hydrogen, which reduces only the chloride of rhodium.

SECTION VI.

RUTHENIUM.

Eq. 52·1 *or* 651·25; Ru.

This metal was discovered by Claus in 1846. It occurs in platinum ores, chiefly in the native osmide of iridium, which contains from 3 to 6 per cent. of it. To separate it, the osmide of iridium is pulverized, mixed with about half its weight of common salt, and heated to low redness in a current of moist chlorine gas. The disintegrated mass is then digested in cold water, and the concentrated solution, which is brown-red and almost opaque, mixed with a few drops of ammonia and gently heated, whereupon it deposits a copious black-brown precipitate, consisting of sesquioxide of ruthenium and bioxide of osmium. This precipitate, after being washed with nitric acid, is heated in a retort, till the osmium is expelled in the form of osmic acid. The residue is then ignited for an hour in a silver crucible with caustic potash free from silica, and the ignited mass softened and dissolved by cold distilled water. The solution is left in a corked bottle for two hours to clarify; after which the perfectly transparent orange-coloured liquid is separated by a siphon, and neutralized with nitric acid. It then deposits velvet-black sesquioxide of ruthenium, which, when washed, dried, and ignited in an atmosphere of hydrogen, yields the pure metal.

Ruthenium is a grey metal, very much like iridium. Its specific gravity is 8·6.* It is very brittle, does not fuse even in the flame of the oxy-hydrogen blowpipe, and is scarcely attacked by aqua-regia. It combines with oxygen in four proportions, forming the three oxides, RuO, Ru_2O_3, RuO_2, and ruthenic acid, RuO_3. Its affinity for oxygen is greater than that of any of the other platinum metals, except osmium. When heated to redness in the air, it oxidizes readily, forming a bluish black oxide, which does not part with its oxygen at a white heat. When fused with nitre or with cautic potash, it is converted into rutheniate of potash. It is not dissolved by fused bisulphate of potash.

Protoxide of ruthenium, RuO.—Obtained by igniting the protochloride with carbonate of soda, in a stream of carbonic acid gas, and washing the residue with water. It is a blackish grey powder, containing 13·4 per cent. of oxygen. It is insoluble in acids, and consequently its salts have not been directly formed.

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* This is much less than the density usually attributed to iridium (p. 624). It is probable, however, that the two metals do not really differ much in density; for a specimen of porous iridium prepared from the blue oxide, by reduction with hydrogen, exhibited a density of only 9·3 (Claus).

The *Protochloride*, RuCl, is obtained in the anhydrous state, by heating the metal to low redness in a stream of chlorine. It is a black crystalline substance, insoluble in water and acids, and imperfectly decomposed by alkalies. A soluble protochloride appears, however, to be formed by passing hydrosulphuric acid gas through a solution of the sesquichloride.

Sesquioxide of ruthenium, Ru_2O_3.—Pulverulent ruthenium, strongly heated before a powerful blowpipe, turns black, and rapidly absorbs oxygen, 100 parts of the metal increasing to 118 parts; afterwards the oxidation slowly proceeds further till the oxide acquires a blackish blue colour, and contains 23 or 24 parts of oxygen to 100 parts of metal, which is about the proportion required for the sesquioxide. The *hydrated sesquioxide* is formed by precipitating a solution of the sesquichloride with an alkali, by decomposing a solution of rutheniate of potash with nitric acid, or by heating the aqueous solution of the sesquichloride. It is a black-brown powder, which becomes suddenly incandescent when heated. Hydrogen gas reduces it imperfectly at ordinary temperatures. It is insoluble in alkalies, but dissolves in acids, forming orange-yellow solutions. The solution in hydrochloric acid exhibits the following reactions:—*Hydrosulphuric acid* partly precipitates the ruthenium in the form of a black sulphide, but at the same time reduces the sesquichloride to protochloride, the reduction being attended with a change of colour from orange-yellow to a fine azure blue: this reaction is extremely delicate, and very characteristic of ruthenium. *Zinc* effects the same reduction. *Hydrosulphate of ammonia* throws down the greater part of the ruthenium in the form of a black-brown sulphide, not perceptibly soluble in excess. The *caustic alkalies*, *alkaline carbonates*, and *phosphate of soda* precipitate the black sesquioxide, insoluble in excess of the reagent. *Borax* forms no precipitate at first, but, on heating the solution, the hydrated sesquioxide is thrown down. *Sulphurous acid*, *oxalic acid*, and *formiate of soda* do not precipitate the metal, but merely decolourize the solution. *Ferrocyanide of potassium* decolourizes the solution at first, but afterwards turns it bluish green. Acetate of *lead* forms a purple-red precipitate, inclining to black. *Cyanide of mercury* colours the solution blue, and throws down a blue precipitate. Nitrate of *silver* forms a black precipitate, which is a mixture of chloride of silver and sesquioxide of ruthenium; the oxide dissolves, after a while, in the nitric acid, leaving a white residue of chloride of silver; and, if ammonia be then added in excess, the chloride of silver dissolves, and the sesquioxide of ruthenium is reprecipitated; this is also a very delicate reaction. The *chlorides of potassium* and *ammonium* throw down from concentrated solutions, crystalline precipitates of double chlorides, exhibiting a play of colours inclining to violet.

Sesquichloride of ruthenium, Ru_2Cl_3, is obtained in the solid state by evaporating the solution of the sesquioxide in hydrochloric acid. The residue is deliquescent, has a very astringent but not metallic taste, and dissolves in water and alcohol, forming beautiful orange-coloured solutions, but leaving a yellow basic compound undissolved. When heated, it turns green and blue. The dilute solution is resolved by heat into hydrochloric acid and the hydrated sesquioxide (p. 634). The sesquichloride forms double salts with the chlorides of potassium and ammonium, and apparently also with those of sodium and barium.

Bioxide of ruthenium, Ruthenic oxide, RuO_2, is formed by roasting and igniting the bisulphide, or by strongly igniting the sulphate, $RuO_2 . 2SO_3$; the former method yields a black-blue powder, with a tinge of green; the latter, grey particles, with metallic lustre and bluish or greenish iridescence. The *hydrate*, $RuO_2 . 2HO$, is obtained as a gelatinous precipitate by decomposing the bichloride of ruthenium and potassium with carbonate of soda. The precipitate, when dried and heated in a platinum spoon, deflagrates with vivid incandescence, and is scattered about. It dissolves in acids, forming solutions which are yellow when dilute, and rose-coloured when concentrated.

The *bichloride* is not known in the separate state, but forms with chloride of potassium a double salt, $KCl,RuCl_2$, which is obtained by treating the sesquichloride of ruthenium and potassium with aqua-regia. This double salt is very soluble in water, but insoluble in alcohol; its colour is brown, inclining to rose-red. The aqueous solution has a deep rose-colour, strongly resembling that of sesquichloride of rhodium. Hydrosulphuric acid acts but slowly on this solution, producing first a milky turbidity from precipitated sulphur, and afterwards throwing down a yellowish brown sulphide; the solution, however, still retains a deep rose-colour and does not turn blue.

Ruthenic sulphate, $RuO_2 \cdot 2SO_3$.—When the sulphide obtained by treating the sesquichloride with hydrosulphuric acid is digested in moderately strong nitric acid, an orange-yellow solution is formed, which, on evaporation, yields this salt in the form of a yellowish brown amorphous mass. It is deliquescent, and dissolves readily in water. Alkalies added to the solution form no precipitate at first; but, on evaporating, a yellowish brown gelatinous precipitate is obtained, consisting of hydrated ruthenic oxide, and strongly resembling impure rhodic oxide. The solution of this salt does not turn blue when treated with hydrosulphuric acid.

Ruthenic acid, RuO_3, is known only in the form of a potash-salt, which is obtained by igniting ruthenium with a mixture of potash, and nitrate or chlorate of potash. It dissolves in water, forming an orange-yellow solution, which has an astringent taste, colours organic substances black by coating them with oxide, and is decomposed by acids, yielding a precipitate of the sesquioxide.

Sulphides of ruthenium.—This metal probably forms with sulphur a series of compounds analogous to the oxides; but it is difficult to obtain them in a definite state. Sulphur and ruthenium do not combine directly, and the precipitates thrown down by hydrosulphuric acid from the chlorides always contain excess of sulphur. When the sulphide obtained by precipitation from the sesquichloride is heated in an atmosphere of carbonic acid, incandescence and explosion take place, sulphur and water pass off, and a blackish grey metallic powder is left, whose analysis agrees with the formula Ru_2S_3. All the sulphides are dissolved by nitric acid of ordinary strength (Claus).

ESTIMATION AND SEPARATION OF RUTHENIUM.

This metal is precipitated from its solutions in the form of oxide, and generally as sesquioxide, viz. from a solution of the sesquichloride, either by alkalies or by simply heating the solution, and from a solution of rutheniate of potash by nitric acid. The precipitated oxide is reduced to the metallic state by ignition in an atmosphere of hydrogen. As, however, the precipitate generally contains alkali, which cannot be removed by washing, the reduced mass must be treated with water; the liquid filtered from the ruthenium; and the metal, before weighing, must be again ignited and left to cool in an atmosphere of hydrogen, as it oxidizes when heated in the air. Ruthenium has hitherto been found only associated with the metals of the platinum-residues, and from these it is separated by the method described at page 633, depending on the resolution of the aqueous sesquichloride by heat into hydrochloric acid and sesquioxide of ruthenium.

NEW METHOD OF TREATING PLATINUM-RESIDUES.*

When platinum-ore has been exhausted by aqua-regia, a residue is left, commonly known by the name of *osmide of iridium.* This residue is a mixture of two different substances, one of which is scaly, and consists of osmium, iridium, and ruthenium; while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodimm. Now oxide of ruthenium can bear a red heat without decomposing, and osmium is actually

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* Fremy, Compt. rend. xxxviii. 1008; also Traité de Chimie Générale, par Pelouze et Fremy, iii. 452.

roasted by the action of oxygen, producing a volatile acid, just as sulphur and arsenic do; hence the residue of platinum-ore may be decomposed by roasting; and by submitting it to this operation, osmic acid is produced in large quantity and very pure, and oxide of ruthenium is obtained in well-defined crystals. The roasting is performed as follows:—

About 200 grammes of platinum-residue (the scaly and granular alloys together) are heated to bright redness in a porcelain tube placed in a long furnace. Air is drawn through the tube by means of an aspirator, being first made to pass through solution of potash to free it from carbonic acid, and through strong sulphuric acid to remove organic matter. The air thus purified passes over the heated platinum-residue, and forms osmic acid and oxide of ruthenium. The latter crystallizes in the colder parts of the roasting tube, while the more volatile osmic acid is carried forward, first into a series of empty tubes, in which part of it settles in the form of crystals, and then through two bottles filled with solution of potash, which retains the uncondensed vapours: the apparatus terminates with an aspirator. The products of the operation are:—1. Oxide of ruthenium, in violet crystals, the form of which is similar to that of native oxide of iron; 2. Osmic acid, very pure, and sometimes amounting to 40 per cent. of the platinum-residue used; 3. Osmiate of potash, which, by the addition of a few drops of alcohol, may be converted into osmite of potash, a salt from which metallic osmium may be obtained (p. 628); 4. An alloy of iridium and rhodium, which remains in the roasting tube.

This last residue may be used for the preparation of iridium and rhodium. For this purpose, it is calcined in an earthen crucible with four times its weight of nitre, care being taken not to carry the process too far; and the residue is exhausted with boiling water and filtered. A copious precipitate is thereby formed, which remains on the filter, and the filtrate consists of an alkaline liquid, which, when left to evaporate, deposits crystals of osmite of potash, the osmium never being completely removed by the previous roasting.

The precipitate which remains on the filter and retains a considerable quantity of potash, is subjected to the action of aqua-regia, which converts the iridium into chloriridiate of potassium, nearly insoluble in cold water: the action of the aqua-regia must be continued for several hours. The mass is then treated with boiling water, which dissolves the chloriridiate of potassium, the washing being continued till the extract no longer exhibits a brown colour. The solutions are then evaporated, and the chloriridiate of potassium obtained in crystals.

The undissolved portion, which contains the rhodium, is dried, mixed with an equal weight of chloride of sodium, and subjected for three or four hours to the action of dry chlorine at a dull red heat. Chlororhodiate of sodium is thereby formed, and may be obtained, by solution in water and evaporation, in beautiful rose-coloured octohedral crystals, resembling chrome alum.

Rhodium is likewise obtained in another stage of the treatment of platinum-ore. When this ore is treated with aqua-regia a certain quantity of rhodium is dissolved together with the platinum, although rhodium by itself is insoluble in aqua-regia. The solution is evaporated to dryness, the residue dissolved in water, and the solution mixed with sal-ammoniac to precipitate the platinum. The rhodium then remains in solution, together with a small quantity of platinum, to separate which a plate of iron is immersed in the liquid, and the pulverulent mixture of platinum and rhodium thereby precipitated is digested in weak aqua-regia, which dissolves the platinum and leaves the rhodium nearly pure. From this residue, pure well-defined crystals of chlororhodiate of sodium may be obtained in the manner just described (Fremy).

SUPPLEMENT.

HEAT.

EXPANSION OF SOLIDS.

The following determinations of the amount of the cubical expansion of solids for each degree Centigrade, at temperatures not exceeding 100° C., are given by H. Kopp,* the volume of the solid at 0° being taken equal to 1 :—

Table I.—Cubical Expansion of Solids.

Substance.	Formula.	Cubical Exp. for 1° C.	Substance.	Formula.	Cubical Exp. for 1° C.
Copper	Cu	0·000051	Arragonite	$CaO.CO_2$	0·000065
Lead	Pb	0·000089	Calcspar	$CaO.CO_2$	0·000018
Tin	Sn	0·000069	Bitterspar	$\left\{ \begin{array}{c} CaO.CO_2 \\ + MgO.CO_2 \end{array} \right\}$	0·000035
Iron	Fe	0·000037			
Zinc	Zn	0·000089	Iron-spar	$\left\{ \begin{array}{c} Fe(Mn,Mg)O. \\ CO_2 \end{array} \right\}$	0·000035
Cadmium	Cd	0·000094			
Bismuth	Bi	0·000040	Heavy spar	$BaO.SO_3$	0·000058
Antimony	Sb	0·000033	Cœlestin	$SrO.SO_3$	0·000061
Sulphur	S	0·000183	Quartz	SiO_3	0·000042
Galena	PbS	0·000068			0·000039
Zinc-blende	ZnS	0·000036	Orthoclase	$\left\{ \begin{array}{c} KO.SiO_3 \\ +Al_2O_3.3SiO_3 \end{array} \right\}$	0·000026
Iron pyrites	FeS_2	0·000034			0·000017
Rutile	TiO_2	0·000032	Soft soda glass	....	0·000026
Tin stone	SnO_2	0·000016			
Iron-glance	Fe_2O_3	0·000040	Another sort	....	0·000024
Magnetic iron ore	Fe_3O_4	0·000029	Hard potash glass	....	0·000021
Fluor-spar	CaF	0·000062			

The mode of experimenting consisted in taking the specific gravity of the solid substance at a lower and at a higher temperature, by ascertaining the quantity of water together with a known weight of the solid substance, and also the quantity of water alone, which filled a vessel of constant capacity at the different temperatures. The determinations in the instances of iron and glass, and the second determinations of quartz and orthoclase, were made with mercury instead of water, and calculated in a similar manner.

Kopp has also determined the expansion of some other solids, especially near the melting points.† Most bodies, at temperatures near their melting points,

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* Ann. Ch. Pharm. lxxxi. 1.

† Ann. Ch. Pharm. xciii. 129.

exhibit a sudden increase in the rate of expansion. The increase of volume which a substance exhibits in the fused state, as compared with the same substance at lower temperatures, arises, partly from the great expansion which it undergoes as it approaches the melting point, partly from the sudden expansion which takes place in fusing. In some substances, however, only one of these modes of expansion is at all considerable.

Phosphorus (the yellow modification), of sp. gr. 1·826 at 10° C. (50° F.), expands uniformly up to its melting point 44° C. (111·2° F.), at which temperature its volume is 1·017 of the volume of 0° C.; but, at the moment of fusion, it exhibits a sudden expansion amounting to 3·4 per cent., so that its liquid volume at 44° C. is 1·052.

Sulphur (native crystals, sp. gr. 2·069) expands irregularly near its melting point (115° C. or 239° F.). Its volume being 1 at 0° C., is 1·010 at 50° C. (122° F.); 1·037 at 100° C.; 1·096 at 115° C.; at the moment of fusion, the expansion amounts to 5 per cent., the volume then increasing to 1·150.

Wax (bleached beeswax, sp. gr. 0·976 at 10° C.) expands very rapidly as it approaches its melting point (64° C. or 147·2° F.), but only 0·4 per cent. more at the moment of fusion. If the volume at 0° C. is 1, the volume at 50° C. (122° F.), is 1·068; at 60° C. (14·0° F.), is 1·128; at 64° C. (147·2° F.), is 1.161, and increases by fusion to 1·166.

Water expands at the moment of freezing by about 10 per cent. 1·1 volume of ice gives 1 volume of water at 0° C., which, when heated to 4° C. (39·2° F.), contracts to 0·99988, but expands progressively at higher temperatures, its volume at 100° being 1·043,

Solid hydrated salts, on the contrary, expand at the moment of fusion; *e. g.* chloride of calcium ($CaCl+6HO$), by 9·6 per cent.; ordinary phosphate of soda ($2NaO.HO.PO_5+24HO$) and hyposulphite of soda ($NaOS_2O_2+5HO$), each by 5·1 per cent.

Rose's fusible metal (2 parts bismuth, 1 part tin, and 1 part lead, sp. gr 8·906 at 10° C.) expands, when heated from 0° to 59° C. (32° to 138·2° F.), in the ratio of 1 to 1·0027; but contracts when further heated, its volume at 82° C. (179·6° F.) being equal to that at 0° C., and at 95° C. (203° F.) equal to 0·9947; in fusing, between 95° and 98° C., it expands by 1·55 per cent., so that at 98° C. (208·4° F.) its volume is equal to 1·0101. This alloy, therefore, contracts from 59° C. up to its melting point.

EXPANSION OF LIQUIDS.

M. Pierre's researches on this subject have been continued.* The expansions of a great number of liquids have also been determined by H. Kopp.†

Pierre concludes from his experiments that isomeric liquids in general do not contract equally at an equal number of degrees below their respective boiling points; an exception is, however, presented by acetate of methyl ($C_2H_3O.C_4H_3O_3$) and formiate of ethyl ($C_4H_5O.C_2HO_3$), in which the contraction for equal intervals below the boiling points appears to be equal.‡

Table II. exhibits the contractions of several groups of isomeric liquids, at D° centigrade below the boiling point, as determined by Pierre and by Kopp.

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* Annales de Chimie et de Physique, [3], xxi. 118, xxxiii. 119.

† Pogg. Ann. lxxii. 1 and 223; and Ann. Ch. Pharm. xciii. 157; xciv. 257; xcv. 307; xcviii. 367.

‡ The contrary statement originally made by Pierre, and quoted at p. 37, of this work, was founded on an error of calculation.

TABLE II.—EXPANSION OF LIQUIDS.

D.	Aldehyde, $C_4H_4O_2$.		Butyric Acid, $C_8H_8O_4$.		Acetate of Ethyl, $C_8H_8O_4$.		D.
	Pierre (B. P. 22°).	Kopp (20·8°).	Pierre (163°).	Kopp (157°).	Pierre (74·1°).	Kopp (74·3°).	
0	10000	10000	10000	10000	10000	10000	0
10	9817	9830	9872	9867	9846	9843	10
25	9567	9596	9688	9677	9629	9622	25
45	9284	......	9453	9439	9359	9352	45
60	9094	......	9288	9271	9172	9165	60
75	......	......	9128	9112	8996	8988	75
110	......	......	8781	8765	8633	......	110

D.	Chloride of Ethylene, $C_4H_4Cl_2$. Pierre (84·9°).	Mono-chlorinated Chloride of Ethyl, $C_4H_4Cl_2$. Pierre (64·8°).	Mono-chlorinated Chloride of Ethylene, $C_4H_3Cl_3$. Pierre (114·2°).	Bichlorinated Chloride of Ethyl, $C_4H_3Cl_3$. Pierre (74·9°).	Formiate of Ethyl, $C_6H_6O_4$.		Acetate of Methyl, $C_6H_6O_4$.		D.
					Pierre (52·9°).	Kopp (54·9°).	Pierre (59·5°).	Kopp (56·3°).	
0	10000	10000	10000	10000	10000	10000	10000	10000	0
25	9677	9669	9693	9648	9632	9631	9633	9631	25
55	9331	9300	9350	9267	9241	9243	9243	9243	55
80	9068	9003	9090	8988	8953	....	8955	......	80

Expansion of water.—Table III. contains the results obtained by Kopp,* and also those of Pierre as calculated by Frankenheim,† with regard to the expansion of water between 0° and 100° C., the volume at zero being taken as the unit.

TABLE III.—EXPANSION OF WATER.

Temp.	Volume.		Temp.	Volume.	
	Kopp.	Pierre.		Kopp.	Pierre.
—15°C.	....	1·003758	19°	1·001370	
—10	....	1·001658	20	1·001567	1·001594
— 5	....	1·000582	21	1·001776	
0	1·000000	1·000000	22	1·001995	
1	0·999947		23	1·002225	
2	0·999908		24	1·002465	
3	0·999885		25	1·002715	1·002708
4	0·999877		30	1·004064	1·004071
5	0·999883	0·999890	35	1·005697	1·005677
6	0·999903		40	1·007531	1·007512
7	0·999938		45	1·009541	1·009563
8	0·999986		50	1·011766	1·011815
9	1·000048		55	1·014100	1·014360
10	1.000124	1·000148	60	1·016590	1·017118
11	1·000213		65	1·019302	1·019947
12	1·000314		70	1·022246	1·022938
13	1·000429		75	1·025440	1·026078
14	1·000556		80	1·028581	1·029360
15	1·000695	1·000728	85	1·031894	1·032769
16	1·000846		90	1·035397	1·036294
17	1·001010		95	1·039094	1·039925
18	1·001184		100	1·042986	1·043649

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* Pogg. Ann. lxxii. 223.

† Pogg. Ann. lxxxvi. 451.

The maximum density Frankenheim finds, from the same data, to exist at the temperature of 3·86° C. or 38·95° F.; Playfair and Joule* fix the point of maximum density at 3·945° C. or 39·1° F.; Plücker and Gessler,† at 3·8° C. or 38·8° F.

Absolute expansion of mercury.—From numerous measurements of the pressures exerted by columns of mercury of equal height, but different temperatures, Regnault‡ finds that if the volume of mercury at 0° C. be = 1, the volume at t° of the air-thermometer is given by the formula—

$$1 + 0{\cdot}000179007\, t + 0{\cdot}0000000252316\, t^2.$$

Hence, the values in

TABLE IV.—EXPANSION OF MERCURY.

Temp.	Volume.	Temp.	Volume.
50°	1·009013	250°	1·046329
100	1·018153	300	1·055973
150	1·027419	350	1·066743
200	1·036811		

Militzer has also determined the absolute expansion of mercury by similar means, but only at ordinary temperatures, the temperature of the colder column of mercury ranging, in his experiments, between 2° and 4° C., and that of the warmer column between 19° and 23°. The mean coefficient of expansion for 1°, deduced from these experiments, is 0·00017405 ± 0·00000082.§ The experiments of Dulong and Petit (37, 38,) give for 1° the coefficient 0·00018018.

SPECIFIC HEAT.

The specific heat of most bodies is greater in the liquid than in the solid state. The following determinations are by Regnault:—

TABLE V.—SPECIFIC HEAT.

Substance.	Solid.		Liquid.	
	Temperature.	Sp. Heat.	Temperature.	Sp. Heat.
Lead	0° to 100° C.	0·0314	350° to 450° C.	0·0402
Bromine	—78 " —20	0·08432	10 " 48	0·1109
Iodine	0 " 100	0·05412	....	0·10822
Mercury	—78 " —40	0·0247	0 " 100	0·0333
Sulphur	0 " 100	0·2026	120 " 150	0·234
Bismuth	0 " 100	0·03084	280 " 380	0·0363
Zinc	0 " 100	0·0956		
Tin	0 " 100	0·0562	250 " 350	0·0637
Phosphorus	10 " 30	0·1887	50 " 100	0·2120
—— Amorphous	15 " 98	0·1700		
Water	below 0	0·502	0 " 20	1·0000
Crystallized chloride of calcium	below 0	0·345	33 " 80	0·555
Nitrate of soda	0 to 100	0·27821	320 " 430	0·413
Nitrate of potash	0 " 100	0·23875	350 " 435	0·3319

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* Phil. Mag. [3], xxx. 41.

† Pogg. Ann. lxxxv. 238.

‡ "Rélations des Expériences entreprises, pour determiner les principales lois physiques et les données numériques qui entrent dans le calcul des machines à vapeur." Paris, 1847.

§ Pogg. Ann. lxxx. 55.

Table VI. exhibits the specific heats of several liquids as determined by H. Kopp,[*] and by Favre and Silbermann.[†] The second column shows the intervals of temperature in Kopp's determinations. Those of Favre and Silbermann were made by cooling the liquids in a mercurial calorimeter of peculiar construction, from their several boiling points to temperatures nearly equal to that of the surrounding atmosphere.

TABLE VI. — SPECIFIC HEAT.

Liquids.	Temperature.	Sp. Heat.	Observers.
Mercury	44° to 24° C.	0·0332	Kopp.
Iodine	....	0·10822	F. S.
Bromine	45 " 11	0·107	Andrews.
Sulphuric acid	46 " 21	0·343	Kopp.
Wood-spirit	43 " 23	0·645	Kopp.
		0·6713	F. S.
Alcohol	43 " 23	0·615	Kopp.
		0·6438	F. S.
Fusel-oil	44 " 26	0·564	Kopp.
		0·5873	"
Ethal	....	0·5059	F. S.
Ether	....	0·50342	"
Formic acid	45 " 24	0·536	Kopp.
Acetic acid	45 " 24	0·509	"
Butyric acid	45 " 21	0·503	"
Formiate of ethyl	39 " 20	0·513	"
Acetate of methyl	41 " 21	0·507	"
Acetate of ethyl	45 " 21	0·496	"
		0·48344	F. S.
Butyrate of methyl	45 " 21	0·487	Kopp.
		0·49176	F. S.
Valerate of methyl	45 " 21	0·491	Kopp.
Acetone	41 " 20	0·530	"
Benzole	46 " 19	0·450	"
Oil of mustard	48 " 28	0·432	"
Oil of turpentine	....	0·46727	F. S.

The specific heat of water at different temperatures has been determined by Regnault,[‡] from whose experiments it appears that the quantity of heat expressed in *heat-units*[§] which one gramme of water loses in cooling down from $t°$ to 0° C. is given by the formula —

$$Q = t + 0{\cdot}00002\, t^2 + 0{\cdot}0000003\, t^3;$$

and the specific heat C. at the temperature $t°$, that is to say, the quantity of heat required to raise one gramme of water from $t°$ to $(t + 1°)$, is —

$$C = 1 + 0{\cdot}00004\, t + 0{\cdot}0000009\, t^2.$$

From this formula, the following numbers are obtained: —

TABLE VII. — SPECIFIC HEAT.

t.	Q.	C.	t.	Q.	C.
0°	0·000	1·0000	150°	151·462	1·0262
50	50·087	1·0042	200	203·200	1·0440
100	100·500	1·0130	230	234·708	0·0568

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[*] Pogg. Ann. lxxv. 98

[†] Comptes Rendus, xxiii. 524.

[‡] "Rélations," &c. (see note, p. 640), 729.

[§] See page 654.

Specific heat of gases and vapours. — On this subject numerous experiments have been made by Regnault,* who finds, contrary to the statement of Delaroche and Bérard, that the specific heat of a gas does not vary, either with its density or with its temperature. The specific heat of atmospheric air, referred to water as unity is found to be 0·2377 between —30° and +10° C.; it is 0·2379 between 10° and 100°; and 0·2376 between 100° and 225°.

Table VIII. contains Regnault's determinations of the specific heats of a considerable number of gases; in column A, as referred to equal weights (water = 1); in column B, as referred to equal volumes.

TABLE VIII. — SPECIFIC HEAT OF GASES (REGNAULT).

	A.	B.		A.	B.
Oxygen	0·2182	0·2412	Ether	0·4810	1·2296
Nitrogen	0·2440	0·2370	Chloride of ethyl	0·2737	0·6117
Hydrogen	3·4046	0·2356	Bromide of ethyl	0·1816	0·6717
Chlorine	0·1214	0·2967	Sulphide of ethyl	0·4005	1·2568
Bromine	0·0552	0·2992	Cyanide of ethyl	0·4255	0·8293
Nitrous oxide	0·2238	0·3413	Chloroform	0·1568	0·8310
Nitric oxide	0·2315	0·2406	Chloride of ethylene	0·2293	0·7911
Carbonic oxide	0·2479	0·2399	Acetate of ethyl	0·4008	1·2184
Carbonic acid	5·2164	0·3308	Acetone	0·4125	0·8341
Sulphide of carbon	0·1575	0·4146	Benzole	0·3754	1·0114
Sulphurous acid	0·1553	0·3489	Oil of turpentine	0·5061	2·3776
Hydrochloric acid	0·1845	0·2302	Terchloride of phosphorus	0·1346	0·6386
Hydrosulphuric acid	0·2423	0·2886	Chloride of arsenic	0·1122	0·7013
Ammonia	0·5080	0·2994	Chloride of silicon	0·1329	0·7788
Marsh-gas	0·5929	0·3277	Bichloride of tin	0·0939	0·8639
Olefiant gas	0·3694	0·3572	Bichloride of titanium	0·1263	0·8634
Water-vapour	0·4750	0·2950			
Alcohol-vapour	0·4513	0·7171			

LIQUEFACTION.

The melting point of a body appears to be influenced to a minute but certain amount, by the pressure to which it is subjected. W. Thomson,† by enclosing transparent pieces of ice and water in an Oersted's water-compressing apparatus, found that the melting point of the ice was lowered 0·059° C. by a pressure of 8·1 atmospheres, and 0·129° by a pressure of 16·8 atmospheres. Bunsen ‡ has obtained similar results with spermaceti and paraffin.

SPERMACETI.

Pressure in Atmospheres.	Solidifying Point.
1	47·7° C.
29	48·3
96	49·7
141	50·5
156	50·9

PARAFFIN.

Pressure in Atmospheres.	Solidifying Point.
1	46·3° C.
85	48·9
100	49·9

Such results are in conformity with the deductions by J. Thomson § from the mechanical theory of heat.

The *latent heat of water* was found by Regnault, and by Provostaye and Desains, to be 79° C. or 142° F. According to Person, this number denotes the

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* Compt. Rend. xxxvi. 676.

† Phil. Mag. [3], xxxvii. 123.

‡ Pogg. Ann. lxxxi. 562.

§ Edin. Phil. Trans. vol. xvi.

quantity of heat required to convert ice at 0° C. into water, but not the total quantity of the latent heat in the water, inasmuch as a certain additional portion of heat is rendered latent as the temperature of the ice rises from —2° to 0°.* In six experiments on the fusion of ice previously cooled to temperatures between —2° and —21°, the latent heat was found to vary between 79·9 and 80·1, the mean quantity being 80° C., or 144° Fah. Regnault also found greater values for the latent heat of water in proportion as the ice used in the experiments had been cooled to a lower temperature. According to Hess, the true latent heat of water is 80·34° C. = 144·6 Fah. For the specific heat of ice, Hess finds the number 0·533; Person finds 0·48 for the temperatures between —21° and —2°, the specific heat of water being 1.

Table IX. contains the latent heats of fusion, and the melting points of various solids, as determined by Person.†

TABLE IX. — LATENT HEAT OF FUSION.

Substances.	Melting point.	Latent Heat.
Tin	235° C.	14·3
Bismuth	270	12·4
Lead	332	5·15
Alloy, Pb_2, Sn_2, Bi_3	96	5·96
Alloy, Pb Sn_2 Bi	145	7·63
Phosphorus	44·2	4·71
Sulphur	115	9·175
Nitrate of Soda	310·5	62·98
Nitrate of Potash	339	46·18
A mixture of 1 eq. Nitrate of Soda and 1 eq. Nitrate of Potash	219·8	51·4
Phosphate of Soda, 2NaO, HO, PO_5 + 24HO	36·4	66·80
Chloride of Calcium, CaCl, 6HO	28·5	40·70
Bees-wax (yellow)	62·0	43·51
Zinc	423·0	27·46

LATENT HEAT OF VAPOURS.

Water. — It is stated at p. 70, of this work, that the sum of the latent and sensible heats of steam is the same at all temperatures. This is commonly known as Watt's law. Southern, on the other hand, maintained that the latent heat alone is constant at all temperatures. But the late elaborate researches of Regnault‡ have shown that both these statements are incorrect, and that the total quantity of heat (expressed in heat-units§), which a unit of weight of saturated aqueous vapour contains at the temperature $t°$ centigrade, exceeds the amount contained in the same weight of water at 0°, by the quantity —

$$\lambda = 606{\cdot}5 + 0{\cdot}305\, t.$$

If from this, we subtract the quantity of heat which a unit of weight of water at $t°$ contains, beyond that which is contained in the same weight of water at 0° (see Regnault's determinations of the specific heat of water at different tempera-

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* Ann. Ch. Phys. [3], xxx. 73.

† Pogg. Ann. lxx. 300; Ann. Ch. Phys. [3], xxvii, 250.

‡ "Rélations des Expériences," &c. (see Note, p 640), 271; also "Works of Cavendish Society," i. 294.

§ A unit of heat is the quantity required to raise the temperature of a unit of weight (1 gramme, 1 pound, &c.) of water at 0°, by 1° Centigrade.

tures, p. 641), we shall obtain the latent heat L of the vapour of water at the temperature *t*°. The values of λ and L for various temperatures are given in Table X., together with the tensions expressed in millimetres and in atmospheres.

TABLE X. — LATENT HEAT OF STEAM.

Temperature.	Tension.		λ	L.
	mm.	atm.		
0° C.	4·60	0·006	606·5	606·5
50	91·98	0·121	621·7	571·6
100	760·00	1·000	637·0	536·5
150	3581·23	4·712	652·2	500·7
200	11688·96	15·380	667·5	464·3
230	20926·40	27·535	676·6	441·9

The latent heats of the vapours of several other liquids at their boiling points have been determined by Andrews,* and by Favre and Silbermann.† The results are given in —

TABLE XI.— LATENT HEAT OF VAPOURS.

Substances.	Boiling point.	Latent Heat of Vapour.	Observers.
Water	100° at 760 mm.	535·9	Andrews.
"	100	536	F. and S.
Iodine		23·95	"
Bromine	58 " 760	45·60	A.
Sulphurous acid		94·56	F. and S.
Terchloride of phosphorus...	78·5 " 767	51·42	A.
Bichloride of tin	112·5 " 752	3·053	"
Bisulphide of carbon	46·2 " 769	86·67	"
Alcohol	77·9 " 760	202·40	"
"	78·4 "	208·92	F. S.
Wood-spirit	65·8 " 767	263·70	A.
"	66·5	263·86	F. S.
Fusel-oil	132	121·37	"
Ether........................	35·6	91·11	"
"	34·9 " 752	90·45	A.
Amylic ether.	113	69·40	F. S.
Acetic acid	120	101·91	"
Formic acid	100	120·72	"
Valerianic acid	175	103·52	"
Butyric acid	16·4	114·67	F. S
Acetate of ethyl	74	105·80	"
" "	74·6 " 762	92·68	A.
Acetate of methyl	55 " 762	110·20	"
Formiate of ethyl	54·3 " 762	105·30	"
Formiate of methyl	32·9 " 752	117·10	"
Iodide of ethyl	71·3 " 760	46·87	"
Iodide of methyl	42·2 " 752	46·07	"
Oxalate of ethyl	184·4 " 779	72·72	"
Butyrate of methyl	93·0^2 " 779	87·33	F. S.
Ethal	360·0^2	58·48	"
Oil of turpentine	156	68·73	"
Terebene	156	67·21	"
Oil of lemons	165	70·02	"
Hydrocarbons —			
(*a*) $C_{12} H_{12}$	198	59·9	"
(*b*) $C_{15} H_{15}$	255	59·7	"

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* Chem. Soc. Qu. J. i. 27.

† Ann. Ch. Phys. [3], xxxvii. 461.

TENSION OF VAPOURS.

Regnault* has made a vast number of observations on the tension of aqueous vapour in vacuo, between the temperatures of — 32° and + 147·5° C., and given formulæ of interpolation for calculating the tension at any given temperature between those limits.

For temperatures between 0° and 100° the interpolation formula is —

$$\log. e = a + b\alpha^t + c\beta^t;$$

in which t denotes the temperature, e the tension, and a, b, c, α, β are constants whose values are determined by five equations of condition, obtained by substituting in the preceding equation the corresponding observed values of t and e for the temperatures 0°, 25°, 50°, 75°, and 100°. (See Table, p. 74). The values thus obtained are —

$$\log. \alpha = 0{\cdot}006865036 \qquad \log. c = 0{\cdot}6116485$$
$$\log. \beta = \bar{1}{\cdot}9967249 \qquad a = +\,4{\cdot}7384380.$$
$$\log. b = \bar{2}{\cdot}1340339$$

For temperatures below 0°, Regnault adopts the formula —

$$e = a + b\alpha^x;$$

in which —

$$x = t - 32;\ \log. b = \bar{1}{\cdot}4724984;\ \log. \alpha = 0{\cdot}0371566;$$
$$a = +\,0{\cdot}131765.$$

For temperatures above 100° C. the interpolation formula is —

$$\log. e = a - b\alpha^x;\ x = t - 100°;$$

in which —

$$\log. \alpha = \bar{1}{\cdot}9977641;\ \log. b = 0{\cdot}4692291$$
$$a = +\,5{\cdot}8267890.$$

It has not yet been found possible to include the whole series of observations in one formula of interpolation.

From the first and second of these formulæ, the following table of tensions † is calculated for every half degree between — 10° and + 35°. This table (which is the one alluded to in the note at page 93,) is of great utility in hygrometric observations :—

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* Ann. Ch. Phys. [3], xi. 273.

† Ann. Ch. Phys. [3], xv. 138.

Table XII.

Tension of Aqueous Vapour from —10° to +35° C.

Degrees.	Tension.	Diff.	Degrees.	Tension.	Diff.	Degrees.	Tension.	Diff.
	mm.			mm.			mm.	
—10·0	2·078		+ 5·0	6·534		+ 20·0	17·391	0·544
9·5	2·168	0·090	5·5	6·763	0·229	20·5	17·935	0·560
9·0	2·261	0·093	6·0	6·998	0·235	21·0	18·495	0·574
8·5	2·356	0·095	6·5	7·242	0·244	21·5	19·069	0·690
8·0	2·456	0·100	7·0	7·492	0·250	22·0	19·659	0·601
7·5	2·561	0·105	7·5	7·751	0·259	22·5	20·265	0·623
7·0	2·666	0·105	8·0	8·017	0·265	23·0	20·888	0·640
6·5	2·776	0·110	8·5	8·291	0·274	23·5	21·528	0·656
6·0	2·890	0·114	9·0	8·574	0·283	24·0	22·184	0·674
5·5	3·010	0·120	9·5	8·865	0·291	24·5	22·858	0·692
5·0	3·131	0·121	10·0	9·165	0·300	25·0	23·550	0·711
4·5	3·257	0·126	10·5	9·474	0·309	25·5	24·261	0·727
4·0	3·387	0·130	11·0	9·792	0·318	26·0	24·988	0·750
3·5	3·522	0·135	11·5	10·120	0·328	26·5	25·738	0·767
3·0	3·662	0·140	12·0	10·457	0·337	27·0	26·505	0·789
2·5	3·807	0·145	12·5	10·804	0·347	27·5	27·294	0·807
2·0	3·955	0·148	13·0	11·162	0·358	28·0	28·101	0·830
1·5	4·109	0·154	13·5	11·530	0·368	28·5	28·931	0·851
1·0	4·267	0·158	14·0	11·908	0·378	29·0	29·782	0·872
0·5	4·430	0·163	14·5	12·298	0·390	29·5	30·654	0·894
0·0	4·600	0·170	15·0	12·699	0·401	30·0	31·548	0·915
+ 0·5	4·767	0·167	15·5	13·112	0·413	30·5	32·463	0·942
1·0	4·940	0·173	16·0	13·536	0·424	31·0	33·405	0·963
1·5	5·118	0·178	16·5	13·972	0·436	31·5	34·368	0·991
2·0	5·302	0·184	17·0	14·421	0·449	32·0	35·359	1·011
2·5	5·491	0·189	17·5	14·882	0·461	32·5	36·370	1·030
3·0	5·687	0·196	18·0	15·357	0·475	33·0	37.410	1·063
3·5	5·889	0·202	18·5	15·845	0·488	33·5	38·473	1·092
4·0	6·097	0·208	19·0	16·346	0·501	34·0	39·565	1·115
4·5	6·313	0·216	19·5	16·861	0·515	34·5	40·680	1·147
						35.0	41·827	

Regnault has also determined the tensions of several other liquids in vacuo. The results (given in Table XIII.) were obtained either by direct measurement of the elastic forces in vacuo, or by determining the temperature of the vapour of a boiling liquid under the pressure of an artificial atmosphere. The former method was adopted for low, the latter for high temperatures. The series of experiments made by the two methods were, however, in all cases made to include a certain common range of temperature, so that the corresponding curves of tension might overlap each other within that range. With liquids which could be obtained perfectly pure, such as water and sulphide of carbon, the two curves thus obtained were found to coincide exactly; but with alcohol, ether, and still more with chloroform, which are more difficult to purify, the presence of foreign substances gave rise to more or less divergence in the results. Thus the tension of chloroform vapour at 36°, was found to be 342·2 mm. by the first method, and 313·4 mm. by the second. Regnault finds that an extremely small amount of impurity may be detected in this manner.

TABLE XIII.—TENSION OF VAPOURS.

Temperature.	Alcohol.	Ether.	Sulphide of Carbon.	Chloroform.	Oil of Turpentine.
	mm.	mm.	mm.	mm.	mm.
—21° C.	3·12				
—20	3·34	69·2			
—16	………	………	58·8		
—10	6·50	113·2	79·0		
0	12·73	182·3	127·3		2·1
10	24·08	286·5	199·3	130·4	2·3
20	44·00	434·8	298·2	190·2	4·3
30	78·4	637·0	434·6	276·1	7·0
40	134·10	913·6	617·5	364·0	11·2
50	220·3	1268·0	852·7	524·3	17·2
60	350·0	1730·3	1162·6	738·0	26·9
70	539·2	2309·5	1549·0	976·2	41·9
80	812·8	2947·2	2030·5	1367·8	61·2
90	1190·4	3899·0	2623·1	1811·5	91·0
100	1685·0	4920·4	3321·3	2354·6	134·9
110	2351·8	6249·0	4136·3	3020·4	187·3
116	………	7076·2			
120	3207·8	………	5121·6	3818·0	257·0
130	4351·2	………	6260·6	4721·0	347·0
136	………	………	7029·2		
140	5637·7	………	………	………	462·3
150	7257·8	………	………	………	604·5
152	7617·3				
160	………	………	………	………	777·2
170	………	………	………	………	989·0
180	………	………	………	………	1225·0
190	………	………	………	………	1514·7
200	………	………	………	………	1865·6
210	………	………	………	………	2251·2
220	………	………	………	………	2690·3
222	………	………	………	………	2778·5

Vapours of saline solutions.—It is well known that the boiling point of a saline solution is higher than that of pure water, the affinity of the water for the salt being, in fact, an additional obstacle which the heat must overcome before ebullition can take place. Nevertheless, it appeared to Rudberg that the vapours rising from such solutions do not exhibit a higher temperature than steam from boiling water; a result which was attributed to the sudden expansion which the vapour undergoes at the moment of escaping from the liquid. Regnault finds, however, that a thermometer having its bulb immersed in the vapour of a boiling saline solution does not give a correct indication of the temperature of that vapour, because the bulb becomes covered with a film of condensed water, and, therefore, the thermometer exhibits only the temperature due to the boiling of that water. But when proper precautions are taken, by the interposition of screens, to prevent, as far as possible, this deposition of water, the temperature of the vapour appears very nearly equal to that of the liquid. It is, however, extremely difficult to remove this source of error completely.

The observation of the elastic force of a vapour arising from a saline solution appears to afford excellent means of detecting chemical changes in the constitution of the liquid, every such change being indicated by the occurrence of a *singular point* in the curve which represents the law of the tension. For example, in the case of salts, like the sulphates of sodium, copper, iron, manganese, &c., which crystallize at different temperatures with different proportions of water, Regnault suggests that the variations in the tension of the vapour might indicate whether the water is chemically combined with the salt while still in solution, or whether the combination takes place at the moment of crystallization.

Mixtures of vapours and gases. — The law of Dalton, that the tension of any saturated vapour in air is the same for any given temperature as in vacuo, must be received with certain limitations. It has been already stated (p. 91) that Regnault found the tension of saturated aqueous vapour in air to be always somewhat less than in vacuo; the differences, however, seldom exceeding 2 per cent. of the entire value. The following are a few of the results obtained: —

Table XIV.

Temperature.	Observed Tension in Air.	Calculated Tension in Vacuo.	Difference.
	mm.	mm.	
0° C.	4·47	4·60	—0·13
12·59	10·31	10·85	—0·54
15	12·38	12·70	—0·32
21	18·27	18·49	—0·22
24·69	22·70	23·13	—0·40
31	32·97	33·41	—0·44
35·97	43·39	44·13	—0·74
38	48·70	49·30	—0·60

Similar differences are observed with other liquids. With ether the following results are obtained: —

Table XV.

Temperature.	Tension of Ether-vapour.		
	In Air.	In Vacuo.	Difference.
	mm.	mm.	mm.
33·62° C.	705·09	726·0	20·9
30·97	645·52	659·0	13·4
26·52	552·67	559·2	6·5
22·63	479·63	484·0	4·4
20·05	429·69	433·9	4·2
19·99	428·88	433·0	4·1
14·26	337·71	341·0	3·3

In air and in hydrogen gas, the tension of ether vapour was found to be always lower in vacuo, unless the gas was strongly compressed; in carbonic acid gas, which (as a liquid) dissolves ether in considerable quantity, the tension never becomes equal to that in vacuo.

The tension of a vapour in a gas is very much affected by the condensation of the vapour on the sides of the vessel, an effect which takes place considerably below the point of saturation. Regnault is of opinion that Dalton's law with regard to the tensions of vapours in gases could never be strictly true, unless the gas were enclosed in a vessel whose walls were, to a certain thickness, formed of the liquid itself.

Vapours of mixed liquids.—Gay-Lussac found that the tension of the vapour arising from two or more mixed liquids is equal to the sum of the tensions of the vapours which each would produce separately. The more recent experiments of Magnus and of Regnault have shown that this law is true, or nearly true, only when the liquids are quite immiscible, such as benzol and water. When the liquids are mutually soluble, but not in all proportions, the tension of the mixed vapour is much less than the sum of the separate tensions. With ether and water it scarcely differs from the tension of the ether-vapour alone; thus:—

TABLE XVI.

Temperature.	Tension of water-vapour.	Tension of ether-vapour.	Sum of tensions.	Observed tension of mixed vapour.
	mm.	mm.	mm.	mm.
15·66° C.	13·16	361·8	374·96	362·95
24·21	22·47	510·0	532·47	510·08
33·08	37·58	711·1	748·68	710·02

When the mixed liquids dissolve in one another in all proportions, the tension of the mixed vapour is in most cases greater than that of the less volatile, but less than that of the more volatile substance; such, for example, is the case with mixtures of ether and sulphide of carbon. In a mixture of benzol and alcohol, however, the tension of the mixed vapour is greater than that of either of the separate vapours. With this mixture Regnault obtained the results given in—

TABLE XVII.

Temperature.	Tension of vapour.		
	Of the mixture	Of alcohol.	Of benzol.
7·22° C.	43·17	40·4	20·1
9·98	50·22	46·8	24·2
13·11	59·66	54·4	29·2
16·05	69·43	62·7	35·0
18·59	79·35	71·0	41·0

When the liquids do not mix, but dispose themselves in layers, the more volatile liquid forming the lower stratum, and the ebullition being but feeble, the temperature and corresponding vapour-tension agree with Gay-Lussac's law. But with a brisk fire and violent ebullition, the temperature remains nearly at the limit at which the more volatile liquid would boil by itself under the same pressure.

CONDUCTION OF HEAT.

In metals.—From the experiments of Wiedemann and Franz,* it appears that the metals follow each other with regard to their heat-conducting power, in the same order as with regard to their power of conducting electricity; and, moreover, that the numbers which express their relative heat-conducting powers, do not differ from those which express their relative powers of conducting electricity, more than the latter numbers, as determined by different observers, differ from each other.

The heat-conducting power of metals appears also to diminish as their temperature rises.

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* Phil. Mag. [4], vii. 33.

TABLE XVIII.

Metals.	Electric-conducting power according to			Heat-conducting power.
	Riess.	Becquerel.	Lenz.	
Silver	100	100	100	100
Copper	66·7	91·5	73·3	73·6
Gold	59·0	64·9	58·5	53·2
Brass	18·4	......	21·5	23·6
Tin........................	10·0	14·0	22·6	14·5
Iron	12·0	12·35	13·0	11·9
Steel	......	......	......	11·6
Lead	7·0	8·27	10·7	8·5
Platinum	10·5	7·93	10·3	8·4
German silver ...	5·9	......	.....	6·3
Bismuth	......	......	1·9	1·8

Conduction of heat in crystallized bodies.—Bodies of perfectly homogeneous structure conduct heat with equal facility in all directions; so likewise do crystallized bodies belonging to the regular system; but in crystals belonging to any other system, the rate of conduction is different in different directions. This subject has been very ingeniously investigated by Senarmont,* whose method of observation was as follows:—A small tube of platinum was inserted through the centre of a flat cylindrical plate of the crystal, in the direction of the axis, the tube being bent at right angles at the lower extremity and heated by a lamp, and a current of air made to pass through the tube by means of an aspirator. The two bases of the cylindrical plate were covered with wax, which, being melted by the heat, traced on the surface a curve line, whose form was determined by the conducting power of the crystal in different directions. Plates of non-crystalline substances, such as glass and zinc, treated in this manner, gave circles having their centres in the axis of the platinum-tube. On a plate of *calc-spar*, cut perpendicularly to the axis of symmetry (the optic axis), the curves are circles with their centres in the axis. On plates parallel to the direction of natural cleavage, the curves are also circles, having a slight tendency to elongate in the direction of the principal section. On plates cut parallel to the axis of symmetry, and at right angles to one of the faces of the primary rhombohedron, the curves are ellipses, having their transverse diameter in the direction of the axis of symmetry. The ratio of the axes of the ellipse thus formed is 1·118 : 1. Similar results are obtained with quartz, the ratio of the axes being 1·31 : 1; also with crystals belonging to the square prismatic system, such as rutile, idocrase, and subchloride of mercury. In crystals belonging to the right prismatic, oblique prismatic, and doubly oblique prismatic systems,—that is to say, in crystals having two axes of double refraction,—three directions are found at right angles to each other, in which the thermal curves, obtained in the manner above described, are ellipses. Hence it is inferred that:—

1. In crystalline media having two optic axes, supposing the medium to be indefinitely extended in all directions, and a centre of heat to exist within it, the isothermal surfaces are ellipsoids with three unequal axes.
2. In crystals with one optic axis, the isothermal surfaces are ellipsoids of revolution round that axis.
3. In crystals belonging to the regular system, and in homogeneous uncrystallized media, the isothermal surfaces are spherical.

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* Ann. Ch. Phys. [3], xxi. 45.

Uncrystallized bodies, however, acquire axes of different heat-conducting power when their molecular structure is altered by pressure, traction, or hardening. Plates of glass subjected to lateral pressure, and heated in the manner above described, exhibit distinct thermic ellipses, having their shorter axes in the direction of the pressure, that is, of the greatest density (Senarmont). It is well known that glass, and other transparent non-crystalline bodies, when similarly treated, acquire the power of double refraction.

Crystalline media likewise exhibit peculiar characters in the transmission of heat by *radiation* as well as by conduction. Through crystals with one optic axis, heat is radiated in different quantity and also of different quality (p. 56), according as it passes in a direction parallel or perpendicular to that axis. In crystals with two optic axes, the quantity and quality of the transmitted heat differ according as the direction of transmission coincides with one or other of the three axes of elasticity (Knoblauch).*

Conducting power of wood. — The dependence of heat-conduction upon molecular arrangement is exhibited by organic structures as distinctly as by crystalline media. This subject has been very ingeniously investigated by Dr. Tyndall,† who has examined the conducting power of various organic substances, especially of wood. The bodies, cut into cubes of equal size, were enclosed between two chambers filled with mercury, that liquid being confined on the sides next the cube by membranous diaphragms, with which the cube was in close contact. The mercury in one of the chambers was heated by a spiral of platinum wire immersed in it, and connected with a galvanic battery. The heat thus generated was transmitted through the organic substance to the mercury in the other chamber, and the quantity of heat thus communicated in a given time, was measured by means of a thermo-electric couple connected with a galvanometer. By transmitting heat in this manner through cubes of wood in different directions, it was found that:

At all points not situated in the centre of the tree, wood possesses three unequal axes of calorific conduction. The first and principal axis is parallel to the fibres of the wood; the second and intermediate axis is perpendicular to the fibres and to the ligneous layers; and the third, and least axis, is perpendicular to the fibre and parallel to the layers.

These axes of heat-conduction coincide with the axes of elasticity, which Savart discovered by observing the figures of sand formed on plates of wood when thrown into acoustic vibration. The same directions are likewise axes of *cohesion* and of *permeability to liquids.* Wood of any kind may be most easily split by laying the blade of the cutting instrument parallel to the fibres and across the annual rings; the direction of least cohesion is, therefore, perpendicular to the fibres, and parallel or tangenital to the rings. The direction of greatest resistance is parallel to the fibres. With regard to permeability, it is well known that plates of wood cut perpendicularly to the fibres are not fit for the bottoms of casks to hold liquids; also, that in cutting staves for casks, it is indispensable to cut them across the woody layers, the direction parallel to the layers being that of least permeability.

It may, therefore, be stated as a general law, that: *the axes of calorific conduction in wood coincide with the axes of elasticity, cohesion and permeability to liquids, the greatest with the greatest, and the least with the least.*

The heat-conducting power of wood does not bear any definite relation to its density. American birch, which is one of the lightest woods, conducts heat better than any other. Oak and Coromandel wood, which are very dense, conduct nearly as well; but iron-wood, which has the enormous density of 1·426, is very low in the scale of conduction.

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* Pogg. Ann. lxxxv. 169; xciv, 161.

† Phil. Mag. [4], vi. 121.

RELATION BETWEEN HEAT AND MECHANICAL FORCE OR WORK.—DYNAMICAL THEORY OF HEAT.

Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapours evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction shows with equal clearness that motion may be converted into heat. That the rise of temperature thus produced is not due to any change in the heat-capacity of the bodies, is strikingly shown in Davy's experiment of melting ice by rubbing two plates of the substance together *in vacuo* (p. 97); and Count Rumford's observations on the heat produced by the boring of ordnance point to the same conclusion. In these and all similar cases, the heat appears as a direct result of the force expended: the motion is converted into heat.

But the connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact numerical law, a given quantity of the one being always convertible into a determinate quantity of the other. The first approximate determination of this numerical relation — *the mechanical equivalent of heat* — was made by Count Rumford in the following manner: A brass cylinder, enclosed in a box containing a known weight of water at 60° F., was bored by a steel borer made to revolve by horse-power, and the time noted which elapsed before the water was raised to the boiling-point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water, 1° F., is equivalent to 1034 times the force expended in raising a pound weight one foot high, or to 1034 *foot-pounds*, as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessels, or of that which was lost by dispersion during the progress of the experiment.

For the most exact determinations of the mechanical equivalent of heat, we are indebted to the careful and elaborate experiments of Mr. J. P. Joule. From experiments made in the years 1840–43, on the relations between the heat and mechanical power generated by the electric current, Mr. Joule was led to conclude that the heat required to raise the temperature of a pound of water 1° F., is equivalent to 838 foot-pounds; and a nearly equal result was afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too high.

The most trustworthy results are, however, obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases. But, in 1842, Meyer showed that the temperature of water may be raised 22° or 23° F. by agitating it. The warmth of the sea after a few days of stormy weather is also, probably, an effect of fluid friction.

In 1843 Mr. Joule showed that heat is evolved in the passage of water through narrow tubes, and that each degree of heat per pound of water required for its evolution in this way a force of 770 foot-pounds. In subsequent experiments, a paddle-wheel was employed to produce fluid friction, and the equivalents 781·5, 782·1, and 787·6 obtained from the agitation of water, sperm-oil, and mercury respectively.

The apparatus finally employed by Mr. Joule* in the determination of this important constant, by means of the friction of water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 206 shows a vertical, and fig. 207 a horizontal section, was firmly fitted into a copper vessel (A, fig. 208) containing water, in the lid of which were two necks, one for the axis

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* Phil. Trans. 1850, i. 61; Chem. Soc. Qu. J. iii. 316.

to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight sets of stationary vanes, was used for experiments on the friction of mercury. The apparatus for the friction of solids consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a fixed bevelled wheel was pressed by a lever. The wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights suspended by strings from the axes of two wooden pulleys *w*, one of which is shown at *p* (fig. 208), their axes being supported on friction-wheels *d d*; and the pulleys were connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

FIG. 206.

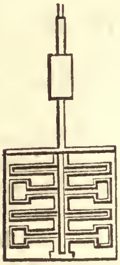


FIG. 207.

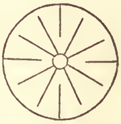
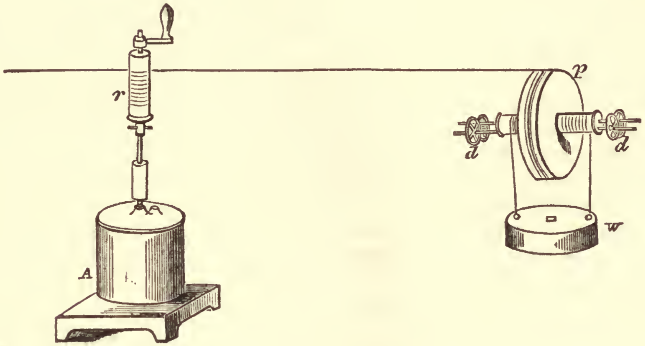


FIG. 208.



The mode of experimenting was as follows: The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained, after which the roller was set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were capable of indicating a variation of temperature as small as $\frac{1}{200}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method, the second column gives the results as they were obtained in air; the third column, the same results corrected for a vacuum.

Material employed.	Equivalent in air.	Equivalent *in vacuo.*	Mean.
Water	773·640	772·692	772·692
Mercury	773·762 776·303	772·814 775·352	774·083
Cast-iron	776·997 774·880	776·045 773·930	774·987

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the frame-work of the apparatus and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because, even in the friction of fluids, it is impossible entirely to avoid vibration and sound.

The conclusions deduced from these experiments are—

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of* 1 *lb. of water (weighed in vacuo, and between* 55° *and* 60°) *by* 1° *F., requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lbs. through the space of* 1 *foot.*

Or, the heat capable of increasing the temperature of 1 *gramme of water by* 1° *cent., is equivalent to a force represented by the fall of* 423·55 *grammes through the space of* 1 *metre. This is consequently the effect of a "unit of heat."*

Kupffer* has also determined the mechanical equivalent of heat by comparing the expansion which a metal wire suffers by heat with the elongation produced by stretching it with a given weight. By this method, which does not appear to be quite so accurate as that above described, it is found that the heat necessary to raise a pound of water 1° Fahrenheit, is equivalent to 661 foot-pounds.

DYNAMICAL THEORY OF HEAT.

The constant relation between heat and work affords a powerful argument in favour of the mechanical or dynamical theory of heat—the theory which rests on the hypothesis that HEAT IS MOTION. This theory has received, of late years, many important additions and developments, chiefly by the labours of Clausius, Joule, Rankine, and W. Thompson. It is impossible, within the limits of this Supplement, to give even a brief account of the whole of these valuable researches; but the leading points of the theory may, perhaps, be sufficiently elucidated by the following summary of two remarkable papers lately published in "Poggendorff's Annalen," one by Krönig, entitled "Fundamental Principles of a Theory of Gases;"† the other, by Clausius, "On the Kind of Motion which we call Heat."‡

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules—each molecule being an aggregate of atoms—are supposed to be constantly moving forward in straight lines, and with a constant velocity, till they impinge against each other or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity, which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected.

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* Phil. Mag. [4], xli. 393.

† Grandzüge einer Theorie der Gase; von A. Krönig. Pogg. Ann. xcix. 315.

‡ Ueber die Art der Bewegung welche wir Wärme nennen; von R. Clausius. Pogg. Ann. c. 353. See also a former paper by Clausius, "Ueber die bewegende Kraft der Wärme," ibid. lxxix. 394.

For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called, by Clausius, *the motion of the constituent atoms* (*Bewegungen der Bestandtheile*). The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the *temperature*. Now, the outward pressure exerted by the gas against the containing envelop, arises, according to our hypothesis, from the impact of a great number of gaseous molecules against the sides of the vessel. But, at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time, must vary inversely as the volume of the given quantity of gas; hence *the pressure varies inversely as the volume, or directly as the density*, which is Mariotte's law.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into the squares of their velocities; in other words, to the so-called *vis viva* or *living force* of the progressive motion. If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a two-fold force, and its number of impacts in a given time will also be doubled; hence the total pressure will be quadrupled.

Now we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by $\frac{1}{273}$ of its bulk for each degree centigrade. Hence the pressure or elastic force increases proportionately to the temperature reckoned from $-273°$ C.; that is to say, to the absolute temperature. Consequently, the *absolute temperature is proportional to the vis viva of the progressive motion.**

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* Suppose a vessel of the form of a rectangular parallelopiped, the length of whose sides are x, y, z, to contain n gas-molecules, each having the mass m. Suppose, also, the space enclosed by this vessel to be divided into $\frac{n}{6}$ equal cubes; and at a given instant let there be in each of these cubes six gas-molecules, moving severally in the directions $+x$, $-x$, $+y$, $-y$, $+z$, $-z$, and with the common velocity c. Let it also be supposed that the molecules exert no mutual action upon each other, but pass without hindrance from side to side of the vessel. It is required to determine the pressure which the gas exerts against one of the sides, yz, of the vessel. The pressure arising from the impact of a single gas-molecule is mca, if a denote the number of impacts which take place in a unit of time. Now, a molecule moving at right angles to yz, or parallel to x, strikes against yz every time that it passes over the space $2x$; therefore $a = \frac{c}{2x}$.

To find the total pressure P upon yz, the quantity, mca, must be multiplied by the number of molecules which move parallel to x, which number, since two atoms out of every six are parallel to x, is $\frac{n}{3}$. Hence $P = m.c.\frac{c}{2x}.\frac{n}{3}$. And the pressure p upon a unit of surface of the side yz, is $p = m.c.\frac{c}{2x}.\frac{n}{3}\frac{1}{yz}$; or if we put $xyz = v$, and leave out the constant factor:

$$p = \frac{nmc^2}{v}.$$

This expression shows that the pressure exerted upon a unit of surface is the same for each side of the vessel; also, that the pressure is inversely in proportion to the volume of the gas, which is Mariotte's law.

The product, mc^2, or the *vis viva* of an atom, is the expression of the temperature reckoned from the absolute zero, or $-273°$ C.

If, in the preceding value of p, we put $mc^2 = t$, we have

$$p = \frac{nt}{v},$$

that is to say, when the volume is constant, the pressure varies directly as the absolute temperature (Krönig).

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and therefore the *vis viva* of the progressive motion must be an aliquot part of the entire *vis viva* of the gas; hence, also, the absolute temperature is proportional to the total *vis viva* arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its temperature by a given amount, is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume, is constant, a result which agrees with the experiments of Regnault, mentioned on pages 141–42. This result may be otherwise expressed as follows: *The total vis viva of the gas is to the vis viva of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution; in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity.

The relations just considered between the pressure, volume and temperature of gases, presuppose, however, certain conditions of molecular constitution, which are, perhaps, never rigidly fulfilled; and accordingly, the experiments of Magnus and Regnault show (40) that gases do exhibit slight deviations from Gay-Lussac and Mariotte's laws. What the conditions are which strict adherence to these laws would require, will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid* state, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately; the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear or rotatory. Moreover, when extraneous forces act upon the body, as in shocks, the molecules may permanently alter their relative positions.

In the *liquid state,* the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules and separate them completely from each other. A molecule is not permanently associated with its neighbours, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory and progressive movement of the molecules, but so regulated, that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous* state, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part, with a velocity equal to that with which they came together. The perfection of the gaseous state, however, implies: 1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas. 2. That the time occupied in the impact of a molecule, either against another molecule, or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts. 3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Mariotte's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced into the liquid state; but to a greater extent with vapours and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position with regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory, and vibratory movements, may be projected from the neighbouring molecules with such force as to throw it completely out of their sphere of action, before its projectile velocity can be annihilated by the attractive force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will, in consequence of the action just described, become more and more filled with these projected molecules, which will comport themselves within it exactly like a gas, impinging and exerting pressure upon the sides of the envelop. One of these sides, however, is formed by the surface of the liquid; and when a molecule impinges upon this surface, it will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained, when the number of molecules projected in a given time into the space above, is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vapourization. The density of the vapour required to ensure the compensation just mentioned, depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the rapidity of their movement within the liquid, that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapour must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There also it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapour-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards, equal to the external pressure tending to compress the vapour-bubble. The boiling point of the liquid will, therefore, be higher as the external pressure is greater.

According to this view of the process of vapourization, it is possible that vapour may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapour must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The *production* and *consumption of heat* which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the *work* done by the acting forces. This work is partly *external* to the body, partly *internal*. To consider first the *internal* work:

When the molecules of a body change their relative positions, the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the *vis viva* of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome, and a corresponding loss of heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a moveable obstacle, such as a piston, the molecules lose just so much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and consequently, the temperature of the gas is raised.

When a liquid is converted into vapour, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being to a considerable extent affected by the external pressure. The liquefaction of a solid not being attended with much increase of volume, involves but little work; nevertheless, the atmospheric pressure does influence, in a slight amount, both the latent heat of fusion and the melting point.

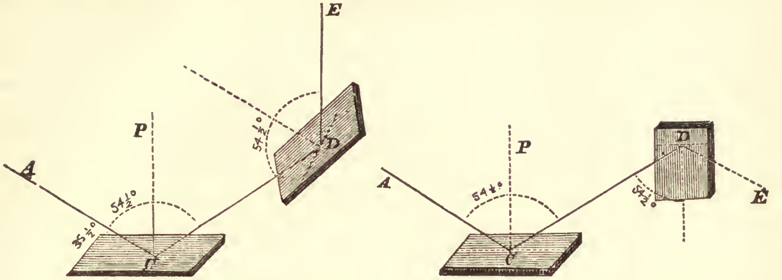
LIGHT.

POLARIZATION.

The phenomena of circular polarization have lately acquired so much importance in chemistry, as to make it highly necessary for the student to be acquainted with them. But to render a description of these phenomena intelligible, a few elementary explanations of the subject of polarization, in general, must first be offered.

Suppose a ray of light, A C (fig. 209), to fall upon a plate of glass (not silvered, but blackened at the lower surface) at C, making an angle of 54½° with the normal P C, or 35½° with the reflecting surface. This ray will be reflected in the direction C D, making an angle P C D = A C P, and in the same plane as A C and C P. Now suppose the reflected ray to fall upon a second surface of glass at the same angle of 54½° with the normal. If, then, the second mirror be so placed, that its plane of reflection is parallel to the plane of reflection from the first surface (see left-hand figure), then the ray will be reflected from the second surface in the direction D E, just as if it proceeded directly from a luminous source, and had not undergone previous reflection; but if the second mirror be so adjusted that its plane of reflection is perpendicular to that of the first (see right-hand figure), then the ray, C D, will not be reflected from it at all. In intermediate positions, still at the same angle of incidence, the ray, C D, will be par-

FIG. 209.



tially reflected, the quantity of light in the reflected ray, D E, being greater as the planes of reflection of the two mirrors are more nearly parallel.

The ray, after reflection from glass at an angle of 54½°, appears then to exhibit different properties, according to the direction in which it is a second time reflected; one side of the ray appearing to be reflectible, and the other side not so. The ray has now different properties on different sides, and is said to be *polarized.*

The angle, 54½°, is called the polarizing angle for glass. For every medium there is a particular polarizing angle, the magnitude of which depends upon the refracting power of the medium.* Now, as the different coloured rays which compose white light, differ in refrangibility (p. 99), there must be for each coloured ray a distinct polarizing angle. Hence it is evident that only homogeneous light can be completely polarized by reflection. Solar light, or ordinary gas or candle-light, can never be made to disappear completely in the manner above mentioned.

The plane in which a polarized ray is most easily reflected is called its *plane of polarization:* it coincides with the plane of reflection (or of incidence).

Light is also polarized by refraction, and the refracted ray is polarized in a plane perpendicular to the plane of refraction, or of incidence, and, therefore, also perpendicular to the plane of polarization of the reflected ray; so that it would be reflected from a surface of glass at an angle of 54½°, just under the circumstances in which the ray polarized by reflection would not. Light, however, is never completely polarized by one refraction; but by successive refractions through a number of surfaces of glass, or other medium, it may be brought within any assigned limit of complete polarization.

All crystalline bodies not belonging to the regular system, possess the power of *double refraction* (p. 99), that is to say, a ray of light entering such a medium

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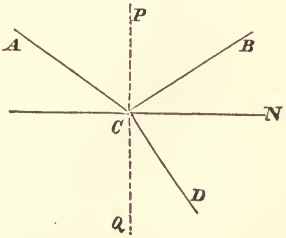
* In all cases, the polarizing angle, A C P (fig. 210), is that for which the refracted ray, C D, is perpendicular to the reflected ray, C B. Let m denote the index of refraction, then:

FIG. 210.



$$m = \frac{\sin \mathrm{ACP}}{\sin \mathrm{QCD}};$$

but angle $\mathrm{ACP} = \mathrm{BCP}\ [=\theta]$; and since B C is perpendicular to C D, and Q C to C N, angle $\mathrm{QCD} = \mathrm{BCN} = 90° - \theta \cdot$ therefore

$$m = \frac{\sin\theta}{\cos\theta} = \tan\theta;$$

that is to say, *the polarizing angle is the angle whose tangent is equal to the index of refraction.*

is split up into two rays of equal intensity, which traverse the crystal in different directions. In all such media, however, there are either one or two directions in which double refraction does not take place, and these lines are called the *optic axes* of the crystal. Transparent calcspar, or Iceland spar, which crystallizes in rhombohedrons, and exhibits double refraction more distinctly than any other substance, is a crystal with one optic axis, the direction of that axis being parallel to the line joining the obtuse summits of the rhomb. A ray traversing the crystal in a direction parallel to this axis is not divided into two; but in all other directions the ray is doubly refracted; and the two rays into which it is thus divided are both completely polarized, the one in the *principal section*, that is to say, in a plane passing through the optic axis and the direction in which the ray traverses the crystal; the other at right angles to that plane. The ray which is polarized in the principal section follows the ordinary laws of refraction, remaining always in the plane of incidence, and having for all incidences a constant index of refraction; but the ray polarized perpendicularly to the principal section follows different laws of refraction, its direction not being confined within the plane of incidence, unless that plane coincides with or is perpendicular to the principal section, and its index of refraction, excepting in the last-mentioned case, varying continually with the angle of incidence. The former of these rays is called the *ordinary*, the latter the *extraordinary* ray.

When these two oppositely polarized rays fall on a plate of glass at the angle of 54½, so placed that the plane of reflection is parallel to the principal section of the crystal, the ordinary ray is reflected, and the extraordinary ray is not, the contrary effect taking place when these planes are at right angles to each other. When the plane of reflection is inclined to the principal section at any angle between 0° and 90°, both rays are reflected, but with different intensities.

Nichol's Prism.—It is often desirable to get rid of one of the images produced by a double-refracting crystal. This is effected by the arrangement shown in fig. 211, which consists of two similar prisms of calcspar, A B C D, C D E F, cemented together with Canada balsam at the faces, C D. The faces, A B, E F, are cut so as to make an angle of 68° with the obtuse edges, A E, B F, of the natural crystal (the natural faces make an angle of 71° with the obtuse edges), and the faces, C D, are perpendicular to A B and E F. With this arrangement, it is found that of the two rays, *n o*, *n e*, into which an incident ray, *m n*, is divided, the ordinary ray, *n o*, on reaching the surface of Canada balsam (whose index of refraction is less than that of the ordinary and greater than that of the extraordinary ray), suffers total reflection in the direction *o* P, while the extraordinary ray passes on in the direction *e f*, and emerges in *f g*, parallel to *m n*. An eye placed at *f*, therefore, sees but one image, viz., that formed by the extraordinary ray. This apparatus, called a Nichol's prism, is of great use in experiments with polarized light. For, as it transmits only the extraordinary ray, a beam of ordinary light passing through it will be polarized in a plane perpendicular to the principal section — that is to say, to the shorter diagonal of the rhomb, *a b* (fig. 212); and a ray, already polarized, will be stopped by the prism if its plane of polarization is parallel to *a b*, but will pass freely through it when the plane of polarization is perpendicular to *a b*, or parallel to the longer diagonal, *c d*. Hence, also, two Nichol's

FIG. 211.

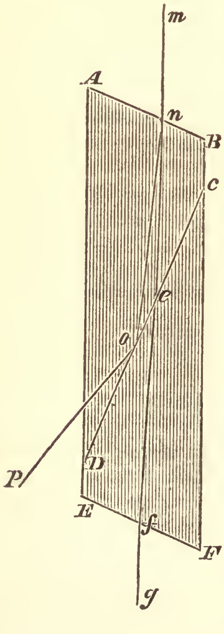
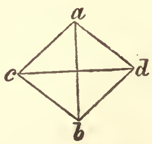


FIG. 212.



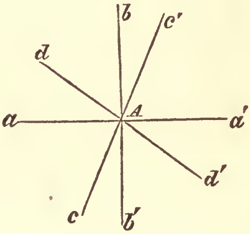
prisms, placed one behind the other, appear perfectly opaque when their principal sections are at right angles to each other, perfectly transparent when the principal sections are parallel, and transmit light with diminished intensity in intermediate positions.

Polarization by Tourmalines.—The tourmaline, which is a crystallized mineral having one optic axis, possesses the remarkable property of transmitting light only when polarized in a plane perpendicular to that axis. Hence, a plate of tourmaline cut with faces parallel to the optic axis, acts exactly like a Nichol's prism, and may be used in the same manner. It is, however, less convenient, on account of its colour, which, in the best tourmalines, is rather a dark yellow-brown.

Nature of Polarized Light. — Light is supposed to consist of undulations excited in an ethereal medium pervading all space, and filling up the intervals between the particles of ponderable bodies. Moreover, the particles of this ether are supposed to vibrate, not in the direction of the ray, like the particles of air in conveying sound, but in planes at right angles to the length of the ray, like the transverse vibrations of a stretched cord.

Further, the difference between ordinary and polarized light, is supposed to be this: that in the former, the particles of the ether vibrate in all imaginable directions, at right angles, to the length of the ray; while, in the latter, they are confined to one particular plane. Thus, if A (fig. 213) represents the projection of an unpolarized ray, travelling at right angles to the plane of the paper, the particles of the ether at all points of this ray vibrate parallel to the plane of the paper, but some may move in the direction *a a′*, others in *b b′*, *c c′*, *d d′*, &c. Now imagine all these vibrations to be reduced to one plane, in the direction *a a′*, for example. Then the ray will become polarized. In fact, since its particles now vibrate in one direction only, it is no longer a matter of indifference whether the ray is presented to a reflecting surface on one side or the other; whereas the unpolarized ray, whose particles vibrate in all directions, will be reflected in the same manner on whichever side it meets the surface of any medium.

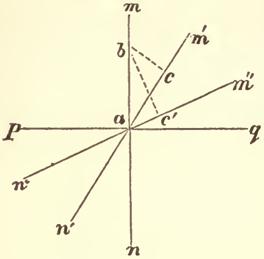
FIG. 213.



Now, from considerations into which we cannot at present enter, it is found that a plate of tourmaline transmits only those vibrations which are parallel to its axis. Since then, a ray of polarized light is transmitted through a tourmaline only when its plane of polarization is perpendicular to the axis of the tourmaline (p. 660), it follows that *the plane of polarization of the ray is perpendicular to the plane of vibration.* Hence, also, the plane of vibration of a ray polarized by reflection is at right angles to the plane of incidence (or of reflection); the plane of vibration of a ray polarized by refraction is parallel to the plane of incidence; and of the two rays into which a beam of light is divided by double refraction through a rhomb of calcspar, the ordinary ray vibrates at right angles to the principal section, and the extraordinary ray parallel to that section. The vibrations of a ray polarized by passing through a Nichol's prism, are, therefore, parallel to the principal section, that is, to the shorter diagonal of the prism (fig. 212).

Let *m n* (fig. 214), be the plane of vibration of a polarized ray moving at right angles to the plane of the paper, and meeting it at the point *a*. If this ray enters a plate of tourmaline, whose axis is parallel to *m n*, or a Nichol's prism, whose principal section is in that direction, the ray will be transmitted with its full intensity. But if the axis of the tourmaline or the principal section of the prism be turned round into the position *m′ n′*, the intensity of the transmitted light will be diminished, because the tourmaline or the prism will only transmit vibrations in the direction am, and there is always a loss of power in changing the direction of motion. Let ab represent the utmost length of the excursion of a particle of the ether in the original direction of vibration, in other words, the original intensity of the light. Draw bc at right angles to am'; then ac represents the component of the force ab in the direction am', and ac is clearly less than ab. If the tourmaline or the prism be turned still further into the position $m'' n''$ the reduced portion of the intensity ac' will be found to be still less; and, lastly, when the axis or the principal section is perpendicular to mn, the reduced portion of the motion becomes equal to nothing, and there is no light transmitted. Generally, if u be the original intensity of the light, and θ the angle between the old and new planes of vibration, the reduced intensity will be $u \cos \theta$.

FIG. 214.



Circular Polarization.—Some media possess the singular property of changing the direction of vibration of a ray of polarized light; in other words, of causing the plane of polarization to rotate through a certain angle, either to the right or to the left. This property is exhibited in a remarkable degree, by quartz or rock-crystal, a mineral which crystallizes in six-sided prisms terminated by six-sided pyramids, the axis being a straight line joining the two pyramidal summits. Suppose now, a ray polarized by passing through a Nichol's prism to be viewed through another such prism, having its principal section at right angles to that of the first. The field will, of course, appear dark. Then let a plate of quartz, bounded by parallel faces cut perpendicularly to its axis, be interposed between the two prisms. Immediately the field of view will appear brilliantly illuminated and coloured, exhibiting a tint of red, yellow, green, blue, &c., according to the thickness of the quartz-plate. If the Nichol's prism, which serves as the eye-piece, be turned on its axis, the colours will go through the regular prismatic series, from red to violet, or the contrary, according to the direction of rotation; but no alteration of colour is produced by rotating the quartz-plate while the eye-piece remains stationary. Exactly similar effects are produced if either of the Nichol's prisms be replaced by a tourmaline or a glass reflector, or a bundle of glass plates which polarize by ordinary refraction; but the two Nichol's prisms form by far the most convenient apparatus, and we shall therefore suppose them to be always used. For distinction, the one is called the polarizing prism or polarizer, the other, the eye-piece.

To understand the phenomena just described, we must examine what takes place when homogeneous light is used. Suppose, then, a plate of dark-red glass coloured with red oxide of copper, to be interposed anywhere between the two prisms placed as before, with their principal sections at right angles, so that no light is transmitted by the eye-piece. On interposing the plate of quartz, a red light immediately makes its appearance, and, to render the field again dark, it is necessary to turn the eye-piece through a certain angle, either to the right or to the left. Now, as the Nichol's prism stops a ray of light only when the plane of vibration of that ray is perpendicular to its principal section, it follows that the ray which has traversed the quartz must have had its plane of vibration thereby deflected through an angle equal to that through which the eye-piece has been moved. This effect is called *circular polarization.*

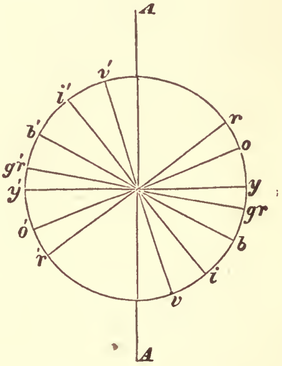
Precisely similar effects are produced with yellow, green, violet, or any other kind of homogeneous light; but the angle of rotation varies according to the nature of the ray, being least for red, and greatest for violet light.

Some crystals of quartz rotate the plane of polarization of a ray to the right, others to the left; the former are called *right-handed*, the latter *left-handed quartz.* But in whichever direction the rotation takes place, a plate of quartz of given thickness always produces the same amount of angular deviation for a ray of given refrangibility; and for plates of different thickness, the deviation for any particular ray increases in direct proportion to the thickness. The following table gives the angles of deviation for the principal rays of the spectrum produced by plates of quartz of the thickness of 1 millimeter and 3·75 millimetres.

Colours.	Angle of rotation.	
	Plate 1 mm. thick.	Plate 3·75 mm. thick.
Medium red	15°	56¼°
" orange	19	71¼
" yellow	24	90
" green	27	101¼
" blue	32	120
" indigo	38	142½
" violet	44	165

We can now explain the succession of colours produced when ordinary daylight is used. Suppose a beam of white light, polarized by a Nichol's prism, whose principal section is parallel to A A′ (fig. 215), to pass through a plate of right-handed quartz, 3·75 mm. thick. The vibrations of the several coloured rays composing the beam of polarized light, are all at first parallel to A A′; but by passing through the quartz, their planes of vibration are deflected through the several angles given in the above table, the red ray then vibrating in the line *r r′*, the yellow in *y y′*, the violet in *v v′*, &c. Now, let the ray be viewed through another Nichol's prism, placed with its principal section also parallel to A A′; then, by reference to the explanation given at page 661, it will be seen that the red and violet rays will be transmitted with but slightly diminished intensity, the orange and blue with less, the yellow with still less, and the green not at all. The result will, therefore, be a purple tint. Now let the eye-piece be turned from left to right. As the principal section passes successively over the lines *r r′*, *o o′*, &c., the red, orange, yellow, &c., will, in succession, be more fully transmitted than the other rays, so that a succession of tints will be produced agreeing nearly with the colours of the spectrum, and following in the same order, from red through yellow to violet. If the eye-piece be turned the contrary way, the order of the tints will be reversed. If the quartz were left-handed, the phenomena would be precisely similar, excepting that the colours would change from red through yellow to violet, when the eye-piece was turned from right to left.

FIG. 215.



Similar changes of colour will be produced with a plate of quartz of any other thickness; but the tint produced at any given inclination of the polarizer and eye-piece, will of course be different.

The tint produced with a quartz plate of 3·75 mm. thick, when the principal sections of the polarizer and eye-piece are parallel to one another, deserves particular notice. This tint, as already observed, is a purple, and moreover changes very quickly to red or to violet, when the eye-piece is turned one way or the other, the change of colour thus produced being, in fact, very much more rapid and decided than in any other part of the circuit. It is accordingly distinguished by the term *sensitive-tint*, or *transition-tint* (*couleur sensible, teinte de passage*). On account of the facility and certainty with which it may be recognized, it is frequently adopted as the standard tint in measuring the angles of rotation produced by different substances; it is, in fact, much easier to determine when this particular colour makes its appearance, than to seize the exact moment when a ray of red, yellow, or other homogeneous light completely disappears.

The rotatory power of quartz is essentially related to its crystalline form. It is not exhibited by opal, or any other amorphous variety of silica, or by silica dissolved in potash or fused by the oxy-hydrogen blowpipe. The same is true with regard to a few other inorganic compounds possessing the rotatory power, viz., chlorate of soda, bromate of soda, and acetate of uranic oxide and soda; these salts exhibiting that power only when crystallized, not in solution.

Circular Polarization in Organic Bodies. — The power of rotating the plane of vibration of a polarized ray, is much more widely diffused in the organic, than in the inorganic world; moreover, inorganic bodies possess it in the liquid, as well as in the crystalline state. Among organic compounds which rotate the plane of polarization to the right, may be mentioned: — Cane-sugar, grape-sugar, diabetic sugar, milk-sugar, dextrin, camphor, asparagin, cinchonine, quinidine, narcotine, tartaric acid, camphoric acid, aspartic acid, oil of lemons, castor-oil, croton-oil. The following rotate to the left: — uncrystallizable sugar of fruits, starch, albumen, amygdalin, quinine, nicotine, strychnine, brucine, morphine, codeine, malic acid, anti-tartaric acid, oil of turpentine, oil of valerian.

By passing a polarized ray through tubes of different lengths, filled with the same solution of cane-sugar, or other rotatory substance, it is found that the angle of deviation is proportional to the length of the column of liquid; and, by filling the same tube with solutions containing different quantities of sugar, &c., it is found that the angle of deviation is proportional to the quantity of the substance contained in a column of given length. Generally, then, the angle of deviation is proportionate to the number of active particles which the light has to pass.

If, then, ε be the quantity of active substance contained in a unit of weight of the solution, l the length of the column, and α the observed angle of rotation for a particular tint, the transition-tint, for example, the angle of rotation for the unit of length, and supposing the entire column to be filled with the optically active substance, will be $\frac{\alpha}{\varepsilon\, l}$. But as the solution of a substance is often attended with condensation of volume, it is best, in order to obtain a measure of the rotatory power, independent of such irregularities, to refer the observed angle of deviation to a hypothetical unit of density, that is to say, to divide the quantity $\frac{\alpha}{\varepsilon\, l}$ by the density δ of the solution. The fraction thus obtained, viz., $[\alpha] = \frac{\alpha}{\varepsilon\, l\, \delta}$, is called the *specific rotatory power*, and expresses the angle of rotation which the pure substance in a column of the unit of length and density = 1 would impart to the ray corresponding to the transition-tint. For example, a solution containing 155 milligrammes of cane-sugar in a gramme of liquid, has a specific gravity = 1·06, and deflects the transition-tint by 24°, in a column 20 centimeters long; its specific rotatory power is therefore —

$$[\alpha] = \frac{24}{0{\cdot}155\,.\,20\,.\,1{\cdot}06} = 7{\cdot}3^\circ$$

Saccharimetry. — An important practical application of the principles just explained relates to the determination of the quantity of sugar contained in saccharine solutions. The apparatus used for this purpose consists of a glass tube (fig. 216), surrounded with a case of wood or brass, and closed at both ends with

Fig. 216.

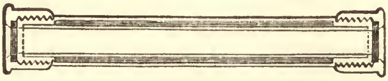
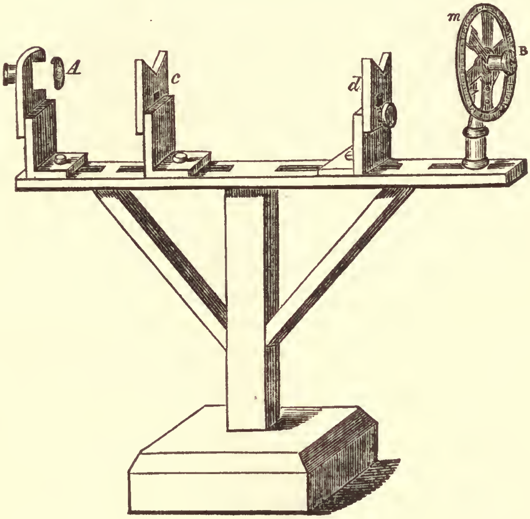


plate-glass discs ground to fit water-tight and pressed against the tube by means of screw-caps. The tube being completely filled with the liquid, is placed on the supports, *c d* (fig. 217), between two Nichol's prisms, one of which, A, serves as a polarizer, the other, B, as an eye-piece. The latter carries a vernier, *m*, moving round a graduated circle. The simplest way of using this apparatus is to interpose between the tube and the polarizer a glass coloured with sub-oxide of copper, the tint of which corresponds with the red of the fixed line C of the spectrum — and having set the eye-piece with its principal section at right angles to that of the polarizer (which makes the field of view dark so long as the tube is not interposed), to adjust the tube in its place, and turn the eye-piece round till the red light completely disappears. The angle through which the eye-piece is turned measures the deviation produced by the saccharine liquid.

FIG. 217.



A solution of 164·71 grammes of pure and dry cane-sugar in a litre of water, produces in a tube, 20 centimetres long, an optical effect equal to that of a plate of right-handed quartz, 1 millimeter thick, that is to say, it turns the plane of polarization of the red ray corresponding to the fixed line C, through an angle of 15·3°. Hence, if any other solution of cane-sugar in a tube of the same length produces a deviation of *a* degrees, one litre of that solution will contain

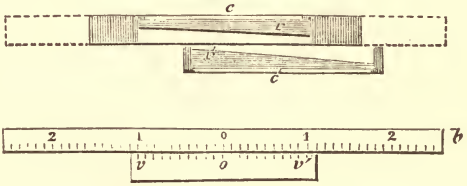
$$\frac{a}{15{\cdot}3} \cdot 164{\cdot}71 \text{ grammes of sugar.}$$

The direct measurement of the rotation of the red ray is, however, by no means the best mode of observation, because, as already observed (p. 664), it is difficult to tell with precision when the light completely disappears. For this reason it is better to introduce behind the polarizing prism, instead of the red glass, a plate of quartz 3·75 millimeters thick, which, when the polarizer and eye-piece are set with their principal sections parallel, exhibits the *transition-tint*. The interposition of the saccharine liquid, which rotates to the right, causes this tint to change; and the rotation is measured by the number of degrees through which the prism must be turned to restore the transition-tint.

Greater exactness is obtained by using a double plate of quartz 3·75 millimeters thick, one-half being composed of right-handed, the other half of left-handed quartz. Such a plate will exhibit the transition-tint with perfect uniformity on both halves, when the polarizer and eye-piece are set with their principal sections parallel; but on turning the eye-piece to the right, one-half of the plate will incline to red, and the other to blue. The same change will, of course, take place on introducing the tube containing the saccharine liquid; and to restore the uniformity of tint, the eye-piece must be turned a certain number of degrees the contrary way. If the liquid has but a slight rotatory power, this method is quite satisfactory; but if the rotatory power is considerable, an error arises from the different angles of rotation imparted to the different coloured rays.

To obviate this last source of inaccuracy, a contrivance, called the *compensator*, has been invented. It consists of two prismatic plates of quartz, *r r′* (fig. 218), having their faces, *c c*, perpendicular to the crystallographic axis, and the opposite faces inclined to this axis at equal angles. These prisms are introduced into the polarizing apparatus between the tube and the eye-piece, and one of them is made to slide over the other by means of a rack and pinion, so that the two together form a plate of variable thickness. To the frame of one of these prisms is attached a linear scale, *a b*, and to the other an index, or a vernier, *v v′*. One hundred divisions of the scale correspond to an increase of 1 millimeter in the thickness of the compound plate. Suppose now these two prisms to consist of left-handed quartz; a flat plate of right-handed quartz, whose thickness is equal to that of the two compensating prisms together when the index points to 0°, is likewise introduced between the tube and the eye-piece. This plate then completely neutralizes the action of the compensator, and the effect is the same as if neither the compensator nor the plate of right-handed quartz were introduced, the double quartz-plate (p. 665) still exhibiting the transition-tint on its two halves, when the tube containing the saccharine solution is not in its place. Now let the tube containing the dextro-rotatory saccharine liquid be introduced. Immediately the two halves of the double-plate assume different colours; and to restore the uniformity of tint, the compensator must be shifted so as to give the combined left-handed prisms a greater thickness. Suppose that, to produce this compensation, the index is moved through eighteen divisions of the scale. Then the rotatory action of the liquid in the tube is equal to that of a quartz-plate having a thickness of $\frac{18}{100}$ of a millimeter, that is to say, it turns the red ray through an angle of $15{\cdot}3° \times \frac{18}{100} = 2\frac{3}{4}°$.

Fig. 218.



In order that the preceding method may be directly applied to determine the strength of a solution of any optically active substance, it is necessary: 1. That the solution contain only *one* such substance. 2. That the quantity of the active substance present be proportioned to the angle of rotation. 3. That the rotation of the red ray be known for one given degree of concentration.

Now, in determining the quantity of crystallizable sugar in the syrups obtained from plants, in molasses, &c., a difficulty arises from the presence of other kinds of sugar, viz., glucose, and, more especially, the uncrystallizable sugar of fruits, which rotates to the left. This difficulty may, in most cases, be obviated by boiling the liquid with hydrochloric acid, whereby the crystallizable sugar (cane-sugar) is converted into the lævo-rotatory sugar of fruits, while the other kinds of sugar remain unaltered. The rotatory power of cane-sugar is not sensibly affected by heat; but that of uncrystallizable sugar decreases considerably as the temperature rises. Thus when cane-sugar is heated with hydrochloric acid to 68° C., the resulting fruit-sugar exhibits at different temperatures the following rotatory powers:—

Temperature	10°	15°	20°	25°	30°	35°
Rotatory power (that of cane-sugar) = 100°......	39	36	34	3·15	29	26·5

Suppose, now, a solution of cane-sugar containing 164·71 grammes in a litre, which, in a column 20 centimeters long, deflects the red ray 15·3° to the right, to be heated to 68° C., with $\frac{1}{10}$ of its volume of hydrochloric acid, and the liquid, after cooling to 15° C., to be introduced into the polarizing apparatus in a tube 22 centimeters long, which will contain the same number of atoms of sugar as a tube 20 centimeters long of the liquid before the addition of the acid. The red ray will then be deflected to the left by $0·36 \times 15·3° = 5·5°$. Consequently, the difference in the positions of the eye-piece before and after the conversion will amount to $15·3° + 5·5° = 20·8°$.

If, then, any mixed solution of cane-sugar and uncrystallizable fruit-sugar, containing 164·71 grammes of sugar in a litre, be treated as above, and the difference in the positions in the eye-piece before and after the conversion be 5·2°, the temperature being 15° C., the amount of crystallizable sugar in the mixture is $\frac{5·2}{20·8} \cdot 164·71 = 41·2$ grammes.*

If the mixture contains grape or starch-sugar mixed with cane-sugar, it must be heated to 80° C. before being introduced into the saccharimeter, because the rotatory power of grape or starch-sugar decreases considerably after a while at ordinary temperatures, but quickly attains its minimum value when the liquid is heated to 80°.

If grape or starch-sugar is present, together with uncrystallizable fruit-sugar, the problem is indeterminate, because neither of these sugars has its rotating action reversed by treatment with acids.

The following table contains a few of the results obtained by the method just described. If the liquid to be examined contains nothing but crystallizable sugar, we have merely to look in the last column but one for the number of degrees read off on the compensator; and the corresponding number in the last column gives the number of grammes of sugar in a litre of the liquid. If other optically active substances are present, and inversion is consequently necessary, the results are found by means of the readings in the first six columns.

---

* Let n be the observed deviation before inversion, n' the dextro-rotation produced by the crystallizable sugar, n'' the lævo-rotation produced by the uncrystallizable fruit-sugar. Also, let n_1 be the observed deviation in a column of liquid of the same length, after the liquid has been heated with $\frac{1}{10}$ of its volume of hydrochloric acid; and suppose that a quantity of cane-sugar which produces a deviation of n' to the right, yields, when thus treated, a quantity of uncrystallizable sugar, which produces a deviation of Kn' to the left at 15° C., $K = 0·36$). Then, for the determination of n' and n'', we have the two equations:—

$$n = n' - n''$$
$$\tfrac{10}{9} n_1 = n'' + Kn'$$

A mixture of cane-sugar with starch-sugar or grape-sugar may be treated in exactly the same manner, since only the cane-sugar has its direction of rotation reversed; and in this case, n' and n'' will be determined by the equations:—

$$n = n' + n''$$
$$\tfrac{10}{9} n_1 = n'' - Kn'$$

TABLE FOR THE ANALYSIS OF SACCHARINE SOLUTIONS.*

Sum or difference of the readings before and after the inversion of the sugar, the last reading being made at the temperature of						Degrees.	Grammes of sugar in a litre.
10°	15°	20°	25°	30°	35°		
1·4	1·4	1·3	1·3	1·3	1·3	1	1·64
13·9	13·6	13·4	13.1	12·9	12·6	10	16·47
27·8	27·3	26·8	26·3	25·8	25·3	20	32·94
41·7	40·9	40·2	39·4	38·7	37·9	30	49·41
55·6	54·6	53·6	52·6	51·6	50·6	40	65·88
69·5	68·2	67·0	65·7	64·5	63·2	50	82·35
83·4	81·9	80·4	78·9	77·4	75·9	60	98·82
97·3	95·5	93·8	92·0	90·3	88·5	70	115·29
111·2	109·2	107·2	105·2	103·2	101·2	80	131·76
125·1	122·8	120·6	118·3	116·1	113·9	90	148·23
139·0	136·5	134·0	131·5	129·0	126·5	100	164·71
152·9	150·1	147·4	144·6	141·9	139·1	110	181·18
166·8	163·8	160·8	157·8	154·8	151·8	120	191·65
180·7	177·4	174·2	170·9	167·7	164·4	130	214·21

Relations between Rotatory Power and Crystalline Form.—It has already been observed that silica and a few other inorganic bodies exhibit circular polarization, only when crystallized. Moreover, crystals of the same substance—quartz, for example—which exert opposite actions on polarized light, often exhibit a remarkable opposition in their crystalline forms. Thus, the ordinary form of quartz, the six-sided prism with pyramidal six-sided summits, is sometimes found modified in the manner shown in figs. 219, 220, the solid angles formed by the meeting of two pyramidal with two prismatic faces, being truncated with faces, *a*, obliquely inclined to the faces of the prism; these truncation faces, however, are only six in number, whereas to form a complete holohedral combination (since these faces are unequally inclined to those of the prism), there should be twenty-four of them, two at each of the twelve angles above-mentioned: the form is therefore tetartohedral.† But, further, these tetartohedral faces are not always placed alike,

FIG. 219.

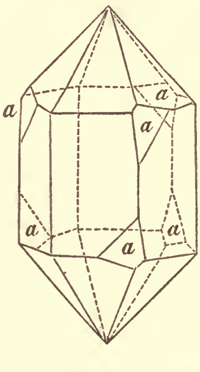
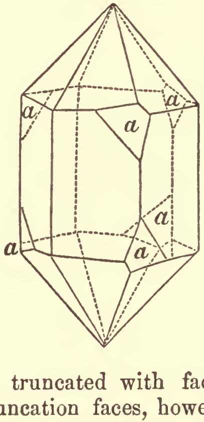


FIG. 220.



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* This table is extracted from the much more extensive one given in the "Traité de Chimie Générale," par Pelouze et Fremy. Paris, 1855, t. iv. pp. 620–622.

† *Holohedral* forms are those which are bounded by similar faces occurring in the greatest possible number consistent with the law of symmetry which determines their position; if the number of such faces is only one-half of what it might be, the form is *hemihedral*; if only one-fourth, it is *tetartohedral.* The regular octohedron is a holohedral crystal, and the tetrahedron is the hemihedral form corresponding to it; similarly, the rhombohedron is the hemihedral form of the double six-sided pyramid. Hemihedral and tetartohedral forms often occur associated with holohedral forms in the same crystal.

occurring in some crystals on the right of a prismatic face above, and on the left below, and the contrary in others, as shown in the above figures. The two forms of crystal thus produced, though their faces are alike in number and in form, are evidently not superposible, but the one may be regarded as the reflected image of the other. Now, the crystals of the one kind invariably exhibit dextro-rotatory, and those of the other kind lævo-rotatory, power. The same kind of opposite tetartohedry, and accompanied by a corresponding opposition of rotatory power, is found in the few other inorganic compounds (p. 664) which exhibit circular polarization.

This remarkable relation between rotatory power and crystalline form is, however, much more strikingly exhibited by certain organic compounds.

Tartaric acid and its salts turn the plane of polarization to the right: racemic acid, which is identical in chemical composition with tartaric acid, and agrees with it in nearly all its chemical relations, has no action whatever on polarized light, either in the free state of the acid or when combined with bases. Now, the crystals of tartaric acid and the tartrates are *hemihedral*, those of racemic acid and the racemates, with one exception, are *holohedral*. The exception alluded to is the racemate of soda and ammonia. A solution of racemate of soda and racemate of ammonia, in equivalent proportions, yields by evaporation crystals of a double salt, the form of which is represented in figs. 221, 222.

Fig. 221.

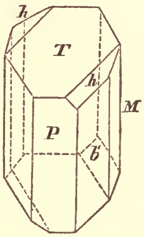
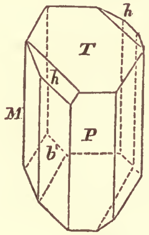


Fig. 222.



It is a right rectangular prism P, M, T, having its lateral edges replaced by the faces b', and the intersection of these latter faces, with the face T, replaced by a face h. If the crystal, were holohedral, there would be eight of these faces, four above, and four below; but, as the figures shows there are but four of them, placed alternately: moreover, these hemihedral faces occupy in different crystals, not similar, but opposite positions; so that, as in the case of quartz, the one kind of crystal is, as it were, the reflected image of the other.

But further; by carefully picking out the two kinds of crystals, and dissolving them separately in water, solutions are obtained, which, at the same degree of concentration, exert equal and opposite actions upon polarized light, the one deflecting the plane of polarization to the right, the other, by an equal amount, to the left. Moreover, the solutions of the right and left-handed crystals, yield, by evaporation, crystals, each of its own kind only; and by mixing the solutions of these crystals with chloride of calcium, lime-salts are obtained, which, when decomposed by sulphuric acid, yield acids, agreeing with each other in composition, and in every other respect, except that their crystalline forms exhibit opposite hemihedral modifications, and their solutions, when reduced to the same degree of concentration, exhibit equal and opposite effects on polarized light.

Of the two acids thus obtained, the one which turns the plane of polarization to the right is identical in every respect with ordinary tartaric acid. The other may be called, for distinction, *antitartaric acid*. When equal weights of these two acids are dissolved in water, and the solutions mixed, a liquid is obtained, which has no action whatever on polarized light, and yields by evaporation, holohedral crystals of *racemic acid.* A similar result is obtained by mixing equal quantities of any of the salts of the two acids, excepting the double salt of soda and ammonia.

Hence it appears that racemic acid, a body which has no action upon polarized light, and crystallizes in holohedral forms, is a compound of two acids (tartaric and antitartaric),* which have equal and opposite effects on polarized light, and crystallize in similar but opposite hemihedral forms. There is also another property in which these acids differ, viz., in their pyro-electric relations. The crystals of both these acids become electric when heated, but the corresponding extremities of the two exhibit opposite electrical states. Racemic acid is not pyro-electric.

Tartaric acid may be converted into racemic acid by the action of heat, provided only it be associated with some substance which will enable it to bear a somewhat high temperature without decomposing. There are many substances whose effect on polarized light is altered by heat. This is remarkably the case with the alkaloids of the cinchona bark. When cinchonine, or any of its salts (which rotate to the right), is heated in such a manner as not to produce decomposition, it is transformed into an isomeric alkaloid, *cinchonicine,* which turns the plane of polarization to the left. Similarly, quinine, which rotates the plane of polarization to the left, is converted by heat into quinicine, which turns it to the right. Now, when tartrate of cinchonine is heated, it is first converted into tartrate of cinchonicine, and if the heat be then continued, the change extends to the tartaric acid, half of which is converted into antitartaric acid. If the process be stopped at a certaint point, and the fused mass treated with water, a solution is obtained which yields, first, crystals of antitartrate, and afterwards, of tartrate of cinchonicine. But if the heat be longer continued, the two acids unite, and form racemate of cinchonicine, from which racemic acid may be prepared, identical in every respect with ordinary racemic acid, and separable by the same means into the two opposite tartaric acids.

But, what is very remarkable, there is formed at the same time a modification of tartaric acid, which has no action whatever on polarized light, and yet is not separable into the two opposite acids. In fact, when the fused mass obtained by heating tartrate of cinchonine is treated with water, and chloride of calcium added, a precipitate is formed, consisting of racemate of lime, and the filtrate, if left at rest, deposits crystals of the lime-salt of *inactive tartaric acid.*

There are other organic compounds which are also optically active in their ordinary forms, but exhibit inactive and inseparable modifications. Malic acid, as it exists in fruits, turns the plane of polarization to the right; so likewise does aspartic acid obtained by the action of acids and alkalies on asparagin. Now both these acids may be formed from fumaric acid, an optically inactive substance. Acid fumarate of ammonia is $C_8H_3(NH_4)O_8 = C_8H_7NO_8$, which is also the formula of aspartic acid, and this acid is actually formed by heating the acid fumarate of ammonia. But the aspartic acid thus produced is, like fumaric acid, optically inactive. Again, aspartic acid is converted into malic acid by the action of nitrous acid:—

$$\underbrace{C_8H_7NO_8}_{\text{Aspartic acid.}} + NO_3 = \underbrace{C_8\,H_6\,O^{10}}_{\text{Malic acid.}} + 2N + HO.$$

Both active and inactive aspartic acids undergo this transformation; but active aspartic acid yields active malic acid, and inactive aspartic acid yields inactive malic acid. Neither inactive aspartic nor inactive malic acid can be separated into two acids oppositely active.

Common oil of turpentine possesses considerable dextrorotatory power; but the

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* Thence also called respectively *dextro-racemic* and *lævo-racemic* acids.

isomeric substance obtained by heating the artificial solid camphor of turpentine with quick-lime is optically inactive.

Fusel oil has lately been shown by Pasteur to be a mixture of two kinds of amylic alcohol, which differ slightly in boiling point. One of these alcohols is optically active, the other inactive.

Rotatory Power induced by Magnetic Action.—Faraday has made the remarkable discovery, that bodies which, in their ordinary state, exert no particular action on polarized light, acquire the circular-polarizing structure when subjected to the action of powerful electric or magnetic forces. A polarized ray passing along the axis of a prism or cylinder of any transparent substance, such as water or glass, has its plane of polarization deflected to the right or left, as soon as the medium is subjected to the action of an electric current passing round it at right angles to the axis, or to that of two powerful opposite magnetic poles, so placed that their line of junction shall be parallel to the axis of the column of the transparent substance. The rotation ceases as soon as the electric or magnetic force ceases to act; its amount varies directly as the strength of the current; and its direction changes with that of the current or of the magnetic force. If the medium has a rotatory power of its own, the total effect is equal to the sum or difference of the natural and induced rotations, according as the electric or magnetic force acts with or against the natural rotatory power of the medium.

CHANGE OF REFRANGIBILITY OF LIGHT.—FLUORESCENCE.

It was observed some years ago by Sir John Herschel, that a solution of sulphate of quinine, though perfectly colourless by transmitted light, exhibits in certain aspects a peculiar blue colour. This blue light was found to be produced only by a very thin stratum of the liquid adjacent to the surface by which the light entered; and the incident beam, after having passed through the stratum from which the blue light came, was not sensibly weakened or coloured, but had lost the power of producing the usual blue colour when admitted into another solution of sulphate of quinine. Light thus modified was said by Sir J. Herschel to be *epipolized.*

Similar phenomena were observed by Sir D. Brewster in an alcoholic solution of chlorophyll, the green colouring matter of leaves, the path of a beam of sunlight admitted into the green solution being marked by a bright light of a blood-red colour. The same appearance was afterwards observed in various vegetable solutions and essential oils, and in some solids. Brewster distinguished this phenomenon by the name of *internal dispersion*, attributing it to the irregular reflection of the light from coloured particles suspended in the liquid, and was of opinion that Herschel's epipolic dispersion was only a particular case of this internal dispersion.

The true explanation of these remarkable phenomena has, however, been given by Professor Stokes,* who has submitted the whole subject to the most searching investigation, and shown that the peculiar dispersion produced by sulphate of quinine, and the other liquids above mentioned, is due *to a change of refrangibility in the rays of light.* The following experiment renders this evident:—

A solar spectrum is formed by means of an achromatic lens, and one or more prisms of flint glass, sufficiently pure to render visible the principal fixed lines, and a tube filled with a solution of sulphate of quinine is passed along this spectrum, from the red towards the violet end. Nothing peculiar is observed while the tube is held in the less refrangible part of the spectrum, the light passing through it freely and without sensible modification; but just before it reaches the extremity of the violet, a peculiar blue diffused light makes its appearance at the surface of the fluid by which the light enters, and remains visible even after the

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* Phil. Trans. 1852, ii. 463.

tube has passed beyond the violet into the invisible portion of the spectrum, acquiring in fact its greatest intensity at a certain distance beyond the extreme violet.

The stratum of liquid from which the diffused blue light emanates is thinner in proportion as the incident rays are more refrangible; and, from a little beyond the extreme violet to the end of the spectrum, the blue space is reduced to an excessively thin stratum adjacent to the surface by which the rays enter. It appears, therefore, that the solution, though transparent with respect to nearly the whole of the visible rays, is of an inky blackness with respect to the invisible rays more infrangible than the violet. Nevertheless, these rays, when once they have been converted into the visible blue light, pass through the liquid with facility. They must, therefore, be essentially altered in character. Now a change in the quality of light must consist, either in a modification of its state of polarization, or in its period of undulation. The former supposition is excluded by the fact that the light thus modified is not polarized at all. It must, therefore, have undergone a change in its rate of vibration, and consequently a change of refrangibility. The existence of this change is, moreover, distinctly proved by examining the diffused light with a prism. It is then found to be by no means homogeneous, but to be resolvable into rays of unequal refrangibility, the whole of which are however comprised within the limits of the visible spectrum. *The diffused blue light consists of the chemical rays rendered visible by a change in their refrangibility.*

The diffusion thus produced is entirely distinct from that which is due to reflection from irregularities or suspended particles. The two phenomena are often produced together in the same medium; but they are easily distinguished by the fact that the light diffused by irregular reflection is more or less polarized, whereas the light diffused in the manner above described is entirely unpolarized, even if the incident rays were themselves polarized. This phenomenon, to which Professor Stokes originally gave the name of *true diffusion*, to distinguish it from the false diffusion produced by irregular reflection, is now called FLUORESCENCE.

It is exhibited by many solutions, and by many solid bodies, opaque as well as transparent, the colour of the diffused light varying with the nature of the medium. An aqueous infusion of horse-chesnut bark exhibits it very strongly, producing the same blue colour as sulphate of quinine. Many compounds of sesquioxide of uranium are also highly fluorescent, and diffuse a greenish-blue light, especially the nitrate, and *canary-glass* (p. 556). A decoction of madder mixed with alum gives a yellow or orange-yellow fluorescence; tincture of turmeric and alcoholic extract of thorn-apple seeds diffuse a greenish light; an alcoholic solution of chlorophyll, a red light.

When the fluorescence is strong, as with sulphate of quinine, it may be seen by merely viewing the substance by ordinary diffused daylight For more accurate observation, and for detecting fluorescence when it exists only in a slight degree, the following method is recommended by Professor Stokes:*—

Light is admitted into a darkened room through a hole several inches in diameter in the window shutter, and the object to be examined is placed on a small shelf, blackened at the top, and fixed just below. The hole is covered with an absorbing medium, called the *principal absorbent*, so selected as to transmit only the feebly luminous and invisible rays of high refrangibility. The body on the shelf is viewed through the second medium, the *complementary absorbent*, which is chosen so as to be as transparent as possible to those rays which are absorbed by the first, and to absorb all the rays which are transmitted by the first. If the media are well selected, they produce a very near approach to perfect darkness; and if the object appears unduly luminous, that effect most probably arises from fluorescence. To determine whether the illumination is really due to that cause, the complementary absorbent is removed from before the eyes to the front of the

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* Phil. Mag. [4], vi. 304.

aperture, when the illumination, if really due to fluorescence, almost wholly disappears; whereas, if it be due merely to scattered light capable of passing through both media, it remains. In examining feebly fluorescent substances, however, it is better to keep the second medium in its place before the eye, and to use a third medium, the *transfer-medium*, placing the last alternately in the path of the incident rays, and between the object and the eye. Still greater delicacy of observation is attained by placing the substance side by side with a small white porcelain tablet, which is quite destitute of fluorescence, and examining the two as above. Or, again, the object being placed on the tablet, a slit is held close to it, in such a position as to be seen projected, partly on the object, partly on the tablet, and the slit is viewed through a prism. The fluorescence of the object is evidenced by light appearing in regions of the spectrum, in which the rays coming through the principal absorbent, and scattered by the tablet, produce nothing but darkness. These methods are delicate enough to show the fluorescence of white paper, even on a very gloomy day.

It is not merely the most refrangible rays that are capable of producing fluorescence; the rays of any part of the spectrum may undergo this change. By examining different media with the spectrum in the manner already described, it is seen that the fluorescence begins, sometimes in the blue, sometimes in the yellow. With an alcoholic solution of chlorophyll, it begins in the red. But wherever the change of refrangibility may begin, it is always in one direction, consisting in a diminution of the index of refractien, and a consequent depression of the light in the scale of colours. In other words, the *length of the wave is increased, and its velocity of undulation diminished.* The vibrations of the ether in the incident ray appear to excite disturbances within the complex molecules of the fluorescent medium, whereby new vibrations are excited in the ether, differing in period from those of the incident ray. The portion of the light which has produced this molecular disturbance is used up, or *absorbed*, and thereby lost to visual perception, just as heat is converted into mechanical work. It is probable that the absorption of light always takes place in this manner. The well-known fact of the conversion of luminous rays into invisible calorific rays, is a striking instance of diminution of refrangibility accompanied by absorption.

As the most refrangible rays are the most active in producing fluorescence, it is natural that this effect should be most strikingly exhibited by the light of flames which are rich in those rays, — the flame of alcohol and of sulphur, for example. These flames do, in fact, produce the effect in a higher degree even than sunlight. An extremely beautiful effect is produced by exposing a number of highly fluorescent media, such as sulphate of quinine, infusion of horse-chesnut bark, and canary-glass, to the flame of sulphur burning in oxygen in a dark room.

The similarity of the blue light diffused by most fluorescent media to the phosphorescence exhibited by certain bodies, might lead us to suppose that the two phenomena proceed from the same cause. Such, however, is not the case: for fluorescence is entirely dependent on the incidence of certain rays, whereas phosphorescence is not; and, moreover, there is no apparent connection between fluorescent and phosphorescent bodies. So far as observation has yet gone, phosphorescent bodies are not fluorescent.

SPECTRA EXHIBITED BY COLOURED MEDIA.

The colour of an object depends upon the rays which it reflects or transmits to the eye; it is, in fact, the mixture or resultant of all the rays which the body does not absorb. We cannot, however, from observation with the unassisted eye, judge with certainty of the rays which are transmitted or reflected; because the same, or nearly the same, compound tint may result from the union of very different primary colours. Thus a body may exhibit an indigo or violet tint, either because it absorbs all the rays excepting those which form the indigo or violet portions of the spectrum, or because it reflects or transmits the red and blue rays in certain proportions; similarly, a green colour may be the pure green of the spectrum, or a mixture of yellow and blue. In such cases, examination with the prism will show of what primary rays the colour is composed, and may thus afford the means of distinguishing between substances which, to ordinary observation, appear of the same colour.

Dr. Gladstone, who has lately made some very interesting observations on the absorption of light by coloured liquids,* introduces the liquid into a wedge-shaped vessel placed before a slit in the window-shutter of a darkened room, so that the line of light may be seen through various thicknesses of the liquid, from the thinnest possible film to a stratum perhaps three-quarters of an inch thick, and examines this line of coloured light with a prism held with its refracting angle parallel to the line of light. The whitish portion of the line, where the light traverses but a thin film of the liquid, is thereby expanded into a spectrum differing but little from that which is given by unaltered daylight; but as the line of light is viewed through deeper portions of the liquid, some rays are seen to diminish in intensity, others gradually to die out, while others almost immediately disappear, giving place to perfect darkness. With a good prism, on a tolerably clear day, the most conspicuous of Fraunhofer's lines may be seen. The appearances presented may be understood from the following representations of the effects produced by solutions of sesquichloride of chromium (fig. 223), and permanganate of potash (fig. 224).† The right-hand side of these figures corresponds with the red extremity of the spectrum: the letters refer to Fraunhofer's lines.

Fig. 223.

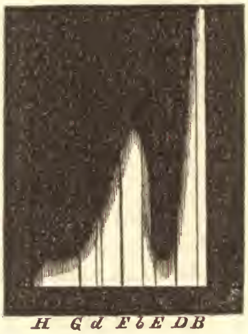
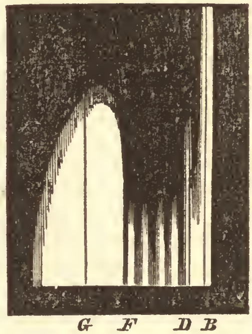


Fig. 224.



A comparison of the spectra exhibited by different salts, only one constituent of which is coloured, shows that, with very few exceptions, all the compounds of the same base or acid have the same effect on the rays of light. This law is seen to hold good in many instances which at first sight appear exceptional. Thus it is well known that some salts of chromic oxide are green, others red or purple. Now these differently-coloured chromic salts all exhibit the same general form of spectrum (fig. 223), in which the violet and indigo rays are very soon cut off; and as the thickness increases, the light is more and more concentrated about two points, one in the red, the other in the bluish green, the red ray penetrating with the greatest facility. Hence it is that the chloride and other salts of chromium, which are green in moderately dilute solutions, appear purple or red when we look through a strong or very deep solution. The acetate absorbs the green rays more readily. and therefore appears green only in very weak solutions, or in thin strata,

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* Chem. Soc. Qu. J. x. 79.

† For representations of the spectra exhibited by a considerable number of coloured liquids, see Dr. Gladstone's paper above referred to.

while the "red potassio-oxalate" absorbs the green so speedily that the thinnest portion of it appears bluish red.

Salts composed of a coloured base and a coloured acid exhibit colours compounded of the rays which are not absorbed by either, the resultant colour bearing, in many instances, but little resemblance to the original colours. Thus, the acid chromate of chromic oxide, a compound of two substances which give respectively yellow and green solutions, is not bright green, but brownish-red, because the chromic acid cuts off nearly all the blue and violet rays, while the oxide of chromium absorbs the yellow and the greater part of the green.

Some salts, which are but slightly coloured, nevertheless exhibit very characteristic spectra. Thus, a solution of sulphate of didymium, which has but a faint rose colour, exhibits, when examined by the hollow wedge and prism, a spectrum containing two very black lines, one in the yellow, the other in the green. These lines are visible in very weak solutions of didymium, and therefore serve as a delicate test for that metal; they moreover afford the means of distinguishing it from cerium and lanthanum, in the spectra of which they do not occur.

MEASUREMENT OF THE CHEMICAL ACTION OF LIGHT.

Chlorine and hydrogen combine under the influence of light, and form hydrochloric acid. Moreover, if the gaseous mixture is in contact with water, the resulting hydrochloric acid is immediately absorbed, and the diminution of volume thus produced affords a measure of the amount of chemical action. This mode of measurement was first adopted by Dr. Draper, of New York, whose experiments led to the important conclusion that *the chemical action of light varies in direct proportion to the intensity of the light, and to the time of exposure.*

But to give to this method all the exactness of which it is susceptible, certain conditions require to be fulfilled; the chief of which are perfect uniformity in the gaseous mixture, constancy of pressure on the gas and liquids throughout the apparatus, and elimination of the disturbing action of radiant heat. These and other essential conditions are completely fulfilled in the apparatus used by Professor Bunsen and Dr. H. Roscoe, in their late elaboratere searches on the chemical action of light.*

This apparatus is represented in figure 225. To furnish the mixture of chlorine and hydrogen gases required, hydrochloric acid is decomposed in the glass vessel *a*, containing two carbon poles, connected by platinum wires with the four-celled Bunsen's battery, C. Between the battery and this vessel is interposed an instrument called the gyrotrope, by means of which the current may be made to pass either directly through the acid vessel *a*, or previously through the vessel *d* containing very slightly acidulated water, whereby the current is greatly weakened, and the evolution of gas in the vessel *a* reduced to a small amount. The mixture of chlorine and hydrogen passes from the vessel *a* through the washing-tube *w*, containing water, then forward through a horizontal tube provided with a glass cock, *h*, into the insolation vessel *i*, where the gases are exposed to the action of light. The lower part of this vessel, containing water, is blackened to protect it from the action of the light. From the insolation vessel, the gas passes through the horizontal measuring-tube K, provided with a millimeter scale, then through the water in the small vessel *l*, and finally into a vessel filled with fragments of charcoal and hydrate of lime, to absorb the excess of chlorine.

When the gas is made to stream through the apparatus, the liquids in *a*, *w*, *i*, and *l*, become gradually saturated with gas; and as the saturation goes on, the composition of the gas varies. At length, however, after the stream of gas has been continued for three or four days, the liquids become saturated, and then the

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* Pogg. Ann. c. 43, 481; abstr. Proceedings of the Royal Society, viii. 235, 236, 516.

evolved gas is found to consist of exactly equal volumes of chlorine and hydrogen. This normal state having been attained, the apparatus is ready for use, and retains its constant sensibility for weeks, requiring only a short saturation each day, previous to the actual observations.

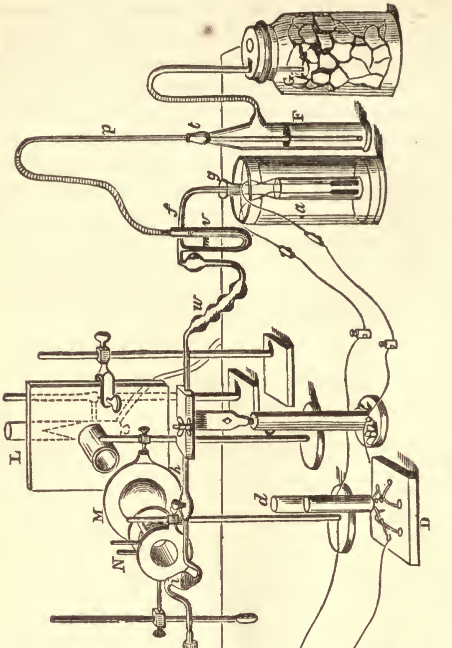


Fig. 225.

To make an observation, the stopcock *h* is closed, and the light allowed to act on the gas in the upper part of the vessel *i*. Combination then takes place, accompanied by diminution of volume, and the external pressure forces the water in *l* through the tube K towards *i*. The position of the end of the column in the scale measures the diminution of volume.

The pressure on the gas in the insolation vessel and the measuring-tube during the observations, is necessarily uniform from the construction of the apparatus; but it is further necessary that uniformity of pressure be ensured in all parts of the apparatus in the intervals between the observations; otherwise the composition of the gaseous mixture will be altered, and the results will no longer be exact. To ensure this uniformity of pressure, the gas, after the stopcock *h* is closed, is made to pass through the bent tube *m v v*, containing water, and thence through the tube *p*, which dips under the water in the vessel F, the pressure being regulated by raising or depressing this tube through the caoutchouc mouth-piece *t*. From the vessel F the gas is conveyed by a flexible tube into the condensing vessel G, containing charcoal and hydrate of lime. As soon as the stopcock *h* is closed, the gyrotrope wire is turned, so as to cause the current to pass through the vessel *d*, and thereby slacken the evolution of gas. When the stopcock *h* is open, the gas will pass one way or the other, according to the depth at which the tube *p* is immersed below the water in F.

To prevent any disturbance from the effects of radiant heat, the light from a coal gas flame, or other source, after being condensed by the convex lens *m*, is made to pass through the cylinder *n*, closed with plate-glass ends, and filled with water. A screen is placed in front of the insolation vessel, to prevent radiation of heat from the body of the observer; and this, together with the screen L, serves also to prevent radiation from external objects. The heat evolved in the insolation vessel by the combustion of the mixed gases, was found by direct experiment, not to exert any sensible influence on the results. All the parts of the apparatus between *a* and *l* are connected by ground-glass joints or by fusing; no caoutchouc, or any other organic matter, which could be acted upon by the chlorine, being introduced, excepting in those parts which merely serve to carry away the waste gas.

Photo-chemical Induction. — On exposing the gas to the light, the quantity of hydrochloric acid formed does not at once attain the maximum: a certain time always elapses before any alternation of volume is perceptible; a slight alteration is, however, soon observed, and this gradually increases till the permanent maximum is reached. This remarkable fact was first observed by Draper, who explained it by supposing that the chlorine underwent, by exposure to light, a permanent allotropic modification, in which it possessed more than usually active properties. But Bunsen and Roscoe have shown that neither chlorine nor hydrogen, when separately insolated, undergoes any such modification, no difference being indeed perceptible between the action of light on a mixture of the gases which have been separately insolated before mixing, and on a mixture of the same gases evolved and previously kept in the dark. The light appears then to act by increasing the attraction between the chemically active molecules, or by overcoming certain resistances which oppose their combination. This peculiar action is called photo-chemical induction.

The time which elapses from the beginning of the exposure till the maximum action is attained, varies considerably according to circumstances, the maximum being sometimes reached in fifteen minutes, sometimes in three or four minutes. In one instance, the first action was visible only after six minutes insolation, whilst in some experiments a considerable action was observed in the first minute.

The duration of the inductive action varies with the mass of the gas, and with the amount of light. With a constant quantity of light, it increases with the volume of the exposed gas. With a constant volume of gas it is found :—1. That the time necessary to effect the first action decreases with increase of light, and in a greater ratio than the increase of light. — 2. That the time which elapses until the maximum is attained, also decreases with increase of light, but in a less ratio. —3. That the increase of the induction proceeds at first in an expanding series, and then converges till the true maximum is attained.

The condition of increased combining power into which the mixture of chlorine and hydrogen is brought by the action of light, is not permanent; on the contrary, the resistance to combination overcome by the influence of the light, is soon restored when the gas is allowed to stand in the dark.

The resistance to combination which prevents the union of the gases until the action is assisted by light, may be increased by various circumstances, especially by the presence of foreign gases, even in very small quantity. An excess of $\frac{3}{1000}$ of hydrogen above that contained in the normal mixture, reduces the action from 100 to 38. Oxygen, in quantity amounting to only $\frac{5}{1000}$ of the total volume of gas, diminishes the action from 100 to 4·7; and $\frac{13}{1000}$ reduces it from 100 to 1·3. An excess of $\frac{10}{1000}$ of chlorine reduces the action from 100 to 60·2; and $\frac{180}{1000}$ from 100 to 41·3. A small quantity of hydrochloric acid gas does not produce any appreciable diminution; $\frac{6}{1000}$ of the non-insolated mixture reduces the action from 100 to 55.

The increase in the rate at which combination goes on up to a certain point under the influence of light, appears to arise, not from any peculiar property of light, but rather from the mode of action of chemical affinity itself. Chemical induction is in fact observed in cases in which there is nothing but pure chemical action to produce the alteration. Thus, when a dilute aqueous solution of bromine mixed with tartaric acid is left in the dark, hydrobromic acid is formed; and, by determining the amount of free bromine present in the liquid at different times, it is found that the rate at which the production of hydrobromic acid goes on is not uniform, but increases up to a certain point, according to a law similar to that which is observed in photo-chemical induction.

These phenomena seem to point to the conclusion that the affinity between any two bodies is in itself a force of constant amount, but that its action is liable to be modified by opposing forces, similar to those which affect the conduction of heat or electricity, or the distribution of magnetism in steel. We overcome these resistances when we accelerate the formation of a precipitate by agitation, or a decomposition by insolation.

Optical and Chemical Extinction of the Chemical Rays. — When light passes through any medium, part of it is lost by reflection at the surface, another portion by absorption within the medium, so that the quantity of emergent light is only a fraction of the incident light. This is true with regard to the chemical as well as to the luminous rays. By passing light from a constant source through cylinders with plate-glass ends filled with dry chlorine, it is found that, with a given length of cylinder, the quantity of the chemical rays transmitted, when no chemical action takes place, is to the quantity in the incident light in a constant ratio; in other words, the absorption of the chemical rays is proportional to the intensity of the light. It is also found that the quantity of chemical rays transmitted varies proportionally to the density of the absorbing medium.

But further, when light passes through a medium in which it excites chemical action, it is found that, in adition to the optical extinction already spoken of, a quantity of light is lost proportional to the amount of chemical action produced. The depth of pure chlorine at 0° C. and 0·76 mm. pressure, through which the light of a coal-gas flame must pass in order to be reduced to $\frac{1}{10}$, is found to be 173·3 millimeters. Hence, since the quantity of light absorbed varies as the density, the depth of chlorine diluted with an equal volume of air, or other chemically inactive gas, required to produce the same amount of extinction, would be 346·6 mm. But when the sensitive mixture of equal volumes of chlorine and hydrogen is used, the depth of the mixture which the light must penetrate to be reduced to $\frac{1}{10}$, is found to be only 234 mm. Hence, it appears that *light is absorbed in doing chemical work.*

With light from other sources, results are obtained similar in character, but differing in amount. Diffuse morning light reflected from the zenith of a cloudless sky is reduced to $\frac{1}{10}$ by passing through 45·6 mm. of chlorine, and through 73·5 mm. of the sensitive mixture; diffuse evening light is reduced to $\frac{1}{10}$ by passing through 19·7 mm. of chlorine and through 57·4 mm. of the standard mixture. Hence it appears that the chemical rays of diffuse morning light are absorbed by chlorine much more quickly than those of lamp-light; and those of evening light with still greater facility. From this we may conclude that the chemical rays reflected at different times and hours, possess, not only quantitative but also qualitative differences, similar to the various coloured rays of the visible spectrum. It is a fact well known to photographers, that the amount of light photometrically estimated gives no measure of the time in which a given photochemical effect is produced. For the taking of pictures, a less intense morning light is always preferred to a bright evening light.

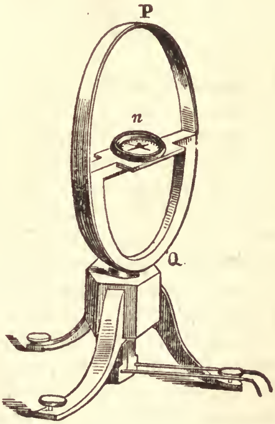
ELECTRICITY.

Measurement of the Force of Electric Currents. — There are two methods by which the forces of electric currents are compared with each other, viz., the *chemical*, or *electrolytic*, and the *electromagnetic methods*.

Faraday has shown that the amount of chemical work done is the same in all parts of the circuit; that, if two decomposing cells be introduced, one containing dilute sulphuric, the other hydrochloric acid, the quantity of hydrogen evolved is the same in both, and equal to the hydrogen evolved (by true current action) in each cell of the battery; moreover, that the quantities of different elements eliminated in any part of the circuit, are always in the ratio of their equivalent weights. The voltameter (p. 221) affords, therefore, a true and exact measure of the amount of the chemical or electrical force developed by the battery. But its indications are not always sufficiently rapid. In fact, in using this instrument, it is necessary to wait till a measurable quantity of gas is collected. It will, therefore, indicate the relative quantity of electricity which has passed through the circuit in a certain finite interval, say in a minute; but it gives no information of any variations that may have taken place during that interval; moreover, it can only be used to measure currents of considerable strength.

The Tangent-compass. — To supply these deficiencies, and obtain exact and instantaneous indications of the relative forces of electric currents, recourse is had to the electro-magnetic method, which consists in observing the deflection of a magnetic needle produced by the current. Instruments for this purpose are called *Galvanometers* or *Rheometers*. The effect of a coil of wire in intensifying the effect of the current upon a magnetic needle, is described at page 221 of this work. But the kind of instrument there described, though commonly called a galvanometer, is really only a galvanoscope, or multiplier. It indicates with great delicacy the existence and direction of an electric current, but it is not constructed for quantitative determinations.

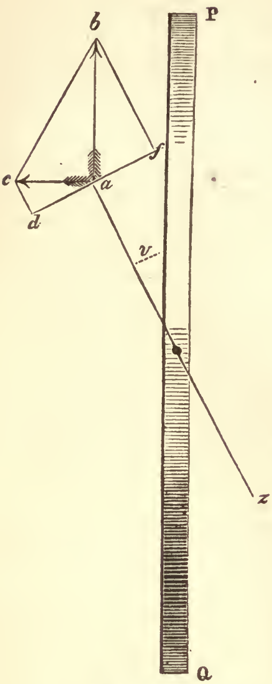
Fig. 226.



In the true galvanometer (Fig. 226) the current, instead of passing through a long coil of wire placed close to the needle, is made to pass through a broad circular band of brass or copper, P Q, of considerable dimensions, in the centre of which is placed a magnetic needle, *n*, the length of which is very small in comparison with the diameter of the circular conductor, so that the distance of the extremity of the needle from the conductor P Q, and consequently the force exerted upon it by the current, is sensibly the same at all angles of deflection. The instrument is so placed that *the plane of the circle* P Q *coincides with the magnetic meridian.* To determine the relation which exists under these circumstances between the deflection of the needle and the force of the current, let P Q (fig. 227) represent the circular conductor seen from above; *a z* the direction of the needle under the influence of the current. The extremity of the needle is then acted upon by two forces, viz., the force of terrestrial magnetism acting parallel to P Q, and the force of the current acting at right angles to that direction. Let these forces be represented in magnitude and direction by the lines *a b*, *a c*. Draw also the line *f a d* perpendicular to $a\,z$, and $b\,f$, $c\,d$, perpendicular to $d\,f$. Then the lines, $a\,f$, $a\,d$, represent the resolved portions of the forces $a\,b$, $a\,c$, which act at right angles to the needle, and tend to turn it one way or the other. In order, therefore, that the needle may be at rest, $a\,d$ must be equal to $a\,f$, or

$$a\,c\,.\,cos\;c\,a\,d = a\,b,\; sin\;a\,b\,f.$$

FIG. 227.



Now the angle $c\,a\,d$ is equal to v, the angle of deflection of the needle from the meridian, because $a\,c$ is perpendicular to P Q, and $a\,d$ to $a\,z$; and the angle $a\,b\,f$ is also equal to v, because $a\,b$ is parallel to P Q, and $b\,f$ to $a\,z$. Hence the preceding equation becomes

$$a\,c\,.\,cos\;v = a\,b\,.\,sin\;v;$$

therefore

$$a\,c = a\,b\,.\,tan\;v.$$

Or, if we denote the force of the earth's magnetism by M, and that of the electric current by E, we have

$$E = M\,tan\;v.$$

Consequently, since the magnetic force of the earth is constant at the same place (at least for short intervals of time), *the magnetic force of the current is proportional to the tangent of the angle of deflection:* hence the name of the instrument.

Comparison between the chemical and magnetic actions of the current. — By introducing into the same voltaic circuit, a voltameter and a tangent-compass, it is found that the *chemical action of the current is directly proportional to its magnetic action.* The tangent-compass affords, therefore, a measure of the chemical as well as of the magnetic force of the current, the quantity of chemical or electrical force in the circuit being proportional to the tangent of the angle of deflection of the needle.

If m milligrammes of hydrogen are evolved in a second in the voltameter, when the galvanometer exhibits a deflection of 45°, and therefore a current force $= 1$ (since $tan\;45° = 1$), then, when the same galvanometer shows a deflection $= \alpha$, the quantity of hydrogen evolved in t seconds will be $m\,.\,t\,.\,tan\;\alpha$. The quantity of any other element eliminated in the same circuit, will be found by multiplying this quantity by the equivalent weight of that element.

With a tangent-compass, the diameter of whose conductor measures one decimeter, it is found that, when the deflection is 45°, one milligramme, or 11·2 cubic centimeters (at 0° C. and Bar. 0·76 met.) of hydrogen is eliminated in 32·3 seconds. Hence with any other circular current whose radius is r decimeters and force $= tan\;\alpha$, the time t in which 1 milligramme of hydrogen is evolved, or 9 milligrammes of water are decomposed, is

$$t = \frac{32{\cdot}3}{r\,.\,tan\;\alpha}.$$

Ohm's Formulæ. — The amount of electrical or chemical power developed in the voltaic circuit, — or, in other words, the quantity of electricity which passes through a transverse section of the circuit, in a unit of time, evidently depends upon two conditions; viz., the power, or electromotive force of the battery, and the resistance offered to the passage of the current by the conductors, liquid or solid, which it has to traverse. With a given amount of resistance, the power of the battery is proportional to the quantity of electricity developed in a given time; and by a double or treble resistance, we mean simply that which, with a given amount of exciting power in the battery, reduces the quantity of electricity developed, or work done, to one-half or one-third. If, then, we denote the electromotive force of the battery by E, and the resistance by R, we have, for the quantity of electricity passing through the circuit in a unit of time, the expression:

$$q = \frac{E}{R} \dots\dots (1)$$

This is called Ohm's law, from the name of the distinguished mathematician who first announced it. It must be understood, not as a theorem, but as a definition. To say that the strength of the current varies directly as the electromotive force, and inversely as the resistance, is simply to define what we mean by electromotive force and what we mean by resistance.*

Let us now endeavour, by means of the formula (1), to estimate the effect produced on the strength of the current by increasing the number and size of the plates of the battery. The resistance R consists of two parts; viz., that which the current experiences in passing through the cells of the battery itself, and that which is offered by the external conductor which joins the poles. This conductor may consist either wholly of metal, or partly of metal and partly of electrolytic liquids. Let the resistance within the battery be r, and the external resistance r'; then, in the one-celled battery, we have

$$q = \frac{E}{r + r'} \dots\dots (2)$$

Now suppose the battery to consist of n cells perfectly similar; then the electromotive force becomes nE, the resistance within the battery nr; if, then, the external resistance remains the same, the strength of the current will be denoted by

$$q = \frac{nE}{nr + r'} = \frac{E}{r + \frac{r'}{n}} \dots\dots (3)$$

If r' be small, this expression has nearly the same value as $\frac{E}{r + r'}$; that is to say, if the circuit be closed by a good conductor, such as a short thick wire, the quantity of electricity developed by the compound battery of n cells, is sensibly the same as that evolved by a single cell of the same dimensions. But if r' is of considerable amount, as when the circuit is closed by a long thin wire, or when an electrolyte is interposed, the strength of the current increases considerably with the number of plates. In fact, the expression (3) is always greater than (2); for—

$$\frac{nE}{nr + r'} - \frac{E}{r + r'} = \frac{(n-1)Er'}{(nr + r')(r + r')};$$

a quantity which is necessarily positive when n is greater than unity.

Suppose, in the next place, that the size of the plates is increased, while their number remains the same. Then, according to the chemical theory, an increase in the surface of metal acted upon must produce a proportionate increase in the quantity of electricity developed, provided the conducting power of the circuit is

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* It must be remembered that we are here merely comparing the strength of electric currents one with the other, not reducing the current force to absolute mechanical measure, or even comparing it with the electro-static forces of attraction and repulsion. (See page 684.)

sufficient to give it passage. According to the theory which attributes the development of the electricity to the contact of dissimilar metals, an increase in the size of the plates does not increase the electromotive force, but it diminishes the resistance within the cells of the battery by offering a wider passage to the electricity. Hence in the single cell, if the surface of the plates, and therefore the transverse section of the liquid, be increased m times, the expression for the strength of the current becomes

$$\frac{E}{\frac{r}{m}+r'}=\frac{mE}{r+mr'}.$$

If r' be small, this expression is nearly the same as $\frac{mE}{r+r'}$, that is to say, the quantity of electricity in the current increases very nearly in the same ratio as the size of the plates; but when the external resistance is considerable, the advantage gained by increasing the size of the plates is much less.

We may conclude, then, that when the resistance in the circuit is small, as in electro-magnetic experiments, a small number of large plates is the most advantageous form of battery; but in overcoming great resistances, power is gained by increasing the number rather than the size of the plates.

Electric Resistance of Metals. — The preceding principles enable us to determine the manner in which the resistance of a metallic wire varies with its length. For this purpose suppose a one-celled battery (Daniell's) to be used, which maintains a constant action during the time of the experiment. First let the current be made to pass directly through the tangent-compass, and afterwards let wires, of uniform thickness and of the lengths of 5, 10, 40, 70, and 100 meters, be interposed in the circuit, and the resulting deflections observed. Now, as the force of the battery is constant, the resistance is inversely as the strength of the current. But the total resistance is made up of that of the interposed wires, together with that of the conductor of the tangent-compass. These last two resistances we may suppose to be equal to that of a wire of the same thickness as the above, and of a certain unknown length, x. Instead, therefore, of the lengths of wire 5, 10, 40, &c., we must substitute $x+5$, $x+10$, $x+40$, &c. An experiment of this kind* gave the following results: —

Length of Wire.	Observed Deflection.	Tangent of Deflection.
x meters	62° 0′	1·880
$x+5$	40 20	0·849
$x+10$	28 30	0·543
$x+40$	9 45	0·172
$x+70$	6 0	0·105
$x+100$	4 15	0·074

Now, let us assume, as most probable, that the resistance of a wire increases in direct proportion to its length, then, according to Ohm's law, the first two experiments give —

$$x : x+5 = 0{\cdot}849 : 1{\cdot}880.$$

whence, $x = 4{\cdot}11$. And, by combining in a similar manner the first experiment with all the others, we obtain for x the several values 4·06, 4·03, 4·14, 4·09, the mean of the whole being 4·08. Substituting this value for x in the preceding table, and calculating the corresponding deflections on the supposition that the strength of the current varies inversely as the resistance, that is as the length of the conductor, we obtain the following results: —

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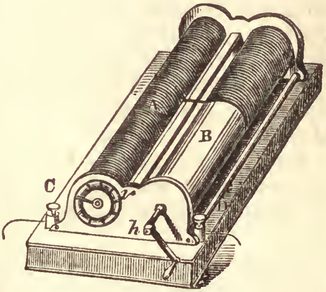
* Müller, Lehrbuch der Physik. 1853, ii. 177.

Length of Conductor.	Calculated Deflection.	Observed Deflection.	Difference.
4·08 meters	62° 0′	62° 0′	
9·08	40 18	40 20	+ 2′
14·08	28 41	28 30	— 11
44·08	9 56	9 45	— 11
74·08	5 57	6 0	+ 3
104·08	4 14	4 15	+ 1

From the results of this and similar experiments, it is inferred that—*the resistance of a conductor of uniform thickness varies directly as its length.*

The Rheostat or Current-regulator.—The various forms of the so-called constant battery, Daniell's for example (p. 218), attain their end but imperfectly, a galvanometer included in the circuit always exhibiting more or less variation. A really constant current can only be obtained by interposing in the circuit a conducting wire of variable length, so that the resistance may be increased or diminished as the action of the battery becomes stronger or weaker. Various instruments have been contrived for this purpose. The one most used, invented by Professor Wheatstone, is represented in fig. 228. A and B are two cylinders of the same dimensions—the first of dry wood, the second of brass—placed with their axes parallel to each other. The wooden cylinder A has a fine screw cut on its surface, and around it, following the thread of the screw, is coiled a thin brass wire. One extremity of this wire, is attached to a brass ring, *v*, at the nearer end of the wooden cylinder, and the other to the farther extremity of the brass cylinder. The ring *v* and the near end of the brass cylinder are connected with the wires of the battery through the medium of the screw-joints C D. A movable handle, *h*, serves to turn the cylinders alternately round their axes. By turning B to the right, the wire is uncoiled from A and coiled upon B; and the contrary when A is turned to the left. The number of coils of wire upon A are indicated by a scale placed between the cylinders, the fractions of a turn being measured by an index moving round the ring *v*, which is graduated accordingly. As the coils of the wire are insulated on the wooden cylinder, but not on the brass, it is evident that the path of the current will be longer, and therefore the resistance greater, in proportion to the number of coils of wire upon the wooden cylinder.

Fig. 228.



By means of the rheostat and the tangent-compass, the resistances afforded by different conductors to the passage of the current may be measured with great facility. Suppose that when the wire of the rheostat is completely uncoiled from the wooden cylinder (the index then standing at 0°), a tangent-compass introduced into the circuit shows a deflection of 46°. Then let a copper wire four yards long and $\frac{1}{20}$th of an inch thick, be introduced into any part of the same circuit. The galvanometer-needle will then exhibit a smaller deflection, say 37°. On removing the wire, the galvanometer will again exhibit its former deflection of 46°. Now let the rheostat wire be coiled round the wooden cylinder till the needle returns to 37°, and suppose that to produce this effect twenty turns of the rheostat wire are necessary. This length of the rheostat wire produces a resistance equal to that of the wire under examination. Next let a similar experiment be made with a wire of the same length but of twice the thickness, and consequently having a transverse section four times as great as that of the former. It will be found that five turns of the rheostat wire, or one-fourth of the former length, are sufficient to produce a resistance equal to that of the second wire. By experiments thus conducted it is found that: *The resistance of a wire or any other conductor of given length varies inversely as its transverse section.* And comparing this result with that which was established at page 682, we find that: *Conductors of the same material offer equal resistances, when their lengths are to one another in the same proportion as their transverse sections.*

In a similar manner, the relative conducting powers of different metals may be ascertained. Taking the resistance of pure copper as the unit, it is found that that of iron is 7·02, of brass 3·95, of German silver 15·47. The conducting powers are of course inversely as these numbers (p. 650).

Heating Power of the Voltaic Current. — The degree of heat excited in a metallic wire by the passage of the current, increases with the strength of the current and with the resistance of the wire. To determine the numerical relations of this phenomenon, the wire to be heated is formed into a spiral and enclosed within a vessel containing strong alcohol, or some other non-conducting liquid, in order that the current may pass entirely through the wire, and not through the liquid itself. The rise of temperature in the liquid is noted by a delicate thermometer; the strength of the current measured by the tangent-compass; and the resistance of the wire afterwards determined in the manner above described. By this method Lenz* has shown that: —

The quantity of heat evolved in a given time is directly proportioned to the resistance of the wire, and to the square of the quantity of electricity which passes through it.

The same result has been obtained by Joule,† both for wires and liquid conductors; by E. Becquerel for liquids; and by Riess‡ for the heat produced by the discharge of the electricity accumulated in a Leyden jar.

Reduction of the Force of the Current to absolute mechanical Measure: — This important determination has been made the subject of an extensive research by Weber and Kohlrausch.§ To understand the results obtained by these philosophers, it is necessary to define exactly the several units of measurement adopted:

a. The unit of electric fluid is the quantity which, when concentrated in a point, and acting on an equal quantity of the same fluid also concentrated in a point, and at the unit of distance, exerts a repulsion equal to the unit of force.

b. The unit of electrochemical intensity is the force of the current which, in a unit of time, decomposes a unit of weight of water, or an equivalent quantity of any other electrolyte.

c. The unit of electromagnetic force, is the force of a current which — when it traverses a circular conductor whose area is equal to the unit of surface, and acts upon a magnet whose magnetic moment is equal to unity, the magnet being placed at a great distance, and in such a manner that its axis is parallel to the plane of the conductor, and its centre on a line drawn through the centre of the circular conductor, and perpendicular to its plane—exerts upon the magnet a rotatory force equal to unity divided by the cube of the distance between the centre of the needle and the centre of the conductor.

Weber had shown by previous experiments that the unit of electrochemical force is to that of electromagnetic force as $106\frac{2}{3}$ to 1. It remained, therefore, to determine the relation between the electromagetic unit and the electrostatic unit

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* Pogg. Ann. lxi. 18.

† Phil. Mag. [3], xix. 210,

‡ Pogg. Ann. xl. 335; xliii. 47; xlv. 1.

§ Abhandlungen der Mathematisch-physischen Classe der Königl. Sachsischen Gesellsch. d. Wiss. Leipzig., 1856.

(1), and thus to establish a numerical relation between statical and dynamical electricity. The mode of experimenting was as follows : —

1. A Leyden jar having been strongly charged, its knob was touched with a large metallic ball, which took from it a certain portion of its charge, determined by previous experiments. The charge of the ball was then transferred to the torsion-balance, and the repulsive force measured. At the same time, the remainder of the charge of the jar was made to traverse the wire of a galvanometer, previously, however, having been passed through a long column of water, in order to give it a sensible duration, and prevent it from passing from one coil of the wire to another in the form of a spark. In this manner, a relation was established between the statical and dynamical effects of the charge of the jar.—2. The intensity and duration of a voltaic current were determined, which imparted to the galvanometer needle the same deflection as that produced by the discharge of the Leyden jar.

The results of the experiments were as follows : —

Through each section of a conductor traversed by a current whose force is equal to the electromagnetic unit, there passes in a second of time a quantity of positive electricity equal to $155,370 \times 10^6$ statical units (p. 684, *a*), and an equal quantity of negative electricity travelling in the opposite direction.

The quantity of electricity required to decompose one milligramme of water, amounts to $106\frac{2}{3}$ times this quantity, or $16,573 \times 10^9$ units of electricity, of each kind. To decompose nine milligrammes of water, or one equivalent, requires of course nine times this amount of electricity. This quantity of positive electricity ($9 \times 16,573 \times 10^9$) accumulated on a cloud situated 1000 meters above the surface of the earth, and acting on an equal quantity of negative electricity on the surface of the earth below the cloud, would exert an attractive force equal to 226,800 kilogrammes, or 208 tons.

From the same data it is calculated that, if all the particles of hydrogen in one milligramme of water in the form of a column one millimeter long, were attached to a thread, and all the particles of oxygen to another thread, then, to effect the decomposition of the water in a second, the two threads would require to be drawn in opposite directions, each with a force of 147,380 kilogrammes, or 145 tons. If the water were decomposed with less velocity, the tension would be proportionally less.

CHEMICAL NOTATION AND CLASSIFICATION.

ATOMS AND EQUIVALENTS.

Equivalent quantities of any two substances are such as can replace one another in combination, producing compounds of similar chemical character. Thus, when copper is immersed in a solution of nitrate of silver, 31·7 parts of copper take the place of 108 parts of silver, forming a neutral nitrate of copper. Similarly, the 31·7 parts of copper may be replaced by 32·5 parts of zinc, and these again by 39 parts of potassium, the product of the substitution being in each case a neutral salt. These quantities of silver, copper, zinc, and potassium, are therefore equivalent to one another: they discharge analogous chemical functions. In like manner, 47 parts of potash, and 31 parts of soda are equivalent, because they unite with the same quantity of an acid to form neutral salts.

Equivalent numbers cannot, however, be always determined by actual substitution. Six parts of carbon are said to be equivalent to 14 parts of nitrogen; but there is no known instance of the direct replacement of nitrogen by carbon. Moreover, certain quantities of sulphuric acid and soda are spoken of as equivalent to one another, although it is plainly impossible that bodies so opposite in character should discharge the same chemical function. In fact, the term equivalent is frequently used, not in its strict etymological sense, but as synonymous with *combining number*. Eight parts of oxygen are said to be equivalent to 1 part of hydrogen, because the bodies unite in this proportion to form water (p. 113). This confusion of the terms equivalent and combining number, arises from the circumstance that the combining numbers in most general use have been selected so as to represent, in many cases, the true equivalents. Nevertheless, the ideas of equivalent and combining proportion are essentially different, and the numbers which relate to them cannot be made to coincide in all cases. The numbers which represent the proportions in which bodies combine, though to a certain extent arbitrary, may be regarded as fixed when once selected; but the equivalent of a body varies according to the chemical function which it discharges. When iron dissolves in hydrochloric acid, producing ferrous chloride, FeCl, every grain of hydrogen expelled from the acid is replaced by 28 grains of iron; but when the same metal dissolves in *aqua regia*, forming ferric chloride, Fe_2Cl_3 or $Fe\frac{2}{3}Cl$, each grain of hydrogen in the acid is replaced by 18⅔ grains of iron; in other words, the equivalent of iron ($H = 1$) is 28 in the ferrous acid, 18⅔ in the ferric compounds. Similarly, the equivalent of mercury is 200 in the mercurous, 100 in the mercuric compounds. By comparing the perchlorates with the permanganates, it appears that 55·7 parts of manganese are equivalent to 35·5 parts of chlorine. Now this same quantity of chlorine is equivalent to 8 parts of oxygen, and to 16 parts of sulphur: moreover, the analogy of the sulphates and manganates shows that 16 parts of sulphur are equivalent to 27·7 parts of manganese, *i. e.*, half the former quantity. Lastly, by comparing the manganous with the manganic salts, it appears that if the equivalent of manganese be 27·7 in the former, it must be 18·5 in the latter. Manganese has, therefore, three different equivalents, according to the kind of compound into which it enters; and, generally, the number of equivalents which may be assigned to a body is equal to the number of chemical functions which it discharges.

The so-called tables of equivalents are really, as already observed, tables of combining proportion. How are these combining proportions determined? Most bodies unite with others in more than one proportion. Eight parts of oxygen combine with 14, 7, 4·7, 3·5, and 2·8 parts of nitrogen. Which of these numbers is to be taken as the combining number of nitrogen? Again, — 1 part of hydrogen unites with 4⅔ parts of nitrogen, and yet the combining number of nitrogen ($H = 1$), is said to be not 4⅔, but three times that number, viz., 14. Why is this last number adopted? The solution of such questions leads to a variety of considerations. Obviously, the combining numbers should be so selected as to represent all series of compounds by the simplest formulæ, and to express analogous combinations by similar formulæ. Practically, however, this rule is not found to be a sufficient guide in all cases; and, in the actual determination of combining numbers, reference is constantly made to considerations intimately related to the atomic theory, such as isomorphism, the specific heat of atoms, vapour-densities, and the basicity of acids. Suppose, for example, the combining number of an acid is to be determined; the first thing to be ascertained is its saturating power. But then arises the question, — is the acid monobasic, bibasic, or tribasic? Now, on the system of combining numbers or equivalents, viewed without reference to atomic constitution, such a question has no meaning. Why, for example, is citric acid said to be tribasic? Because the formula of a neutral citrate is $C_{12}M_3O_{14}$; a formula which does not admit of division by 3, without introducing a fractional number of oxygen-atoms. But if the symbols merely denote combining numbers or equivalents, there can be no valid objection to the use of such fractional numbers. There is nothing absurd in the idea of $\frac{14}{3}$ of the quantity of oxygen which unites with one pound of hydrogen to form water. But if the symbols denote atoms, the case is altered, the idea of a divided atom being self-contradictory.

This is but one instance out of many of the influence exerted by the atomic theory on the construction of chemical formulæ, and consequently on the determination of combining numbers. These numbers do, in fact, represent the supposed relative weights of atoms. Different views may be entertained of the atomic constitution of bodies, and, in the present state of chemical knowledge, the determinations of the atomic weight of a body from different points of view may not always agree: the specific heat, for example, sometimes leading to one conclusion, the vapour-density to another; but the idea of atoms and of their relative weights, and of the building up of compounds by the juxtaposition of elementary atoms, is perfectly definite, and affords the only satisfactory explanation yet given of the observed laws of chemical combination (p. 120).

GERHARDT'S UNITARY SYSTEM.

There are three systems of atomic weight in use among chemists:—1. The system adopted in this work, which is the same as that in Gmelin's Hand-book. In this system, water is represented by the formula HO, and the metallic oxides (protoxides) most resembling it, by the formula MO. The atomic weights correspond, for the most part, with the equivalents, substitution being supposed to take place, atom for atom.

2. The system of Berzelius, based upon the hypothesis that all elementary gases contain equal numbers of atoms in equal volumes, so that the atomic constitution of a compound corresponds with its constitution by volume. Thus, water being composed of 2 vol. H to 1 vol. O, is H_2O; hydrochloric acid, being composed of equal volumes of chlorine and hydrogen, is HCl, &c. The atomic weights in this system are the same as those in the former (p. 102), excepting those of hydrogen, nitrogen, phosphorus, chlorine, bromine, iodine, and fluorine, which have half the values there assigned to them, viz.:—$(O = 8)$; $H = 0{\cdot}5$; $N = 7$; $P = 16{\cdot}01$; $Cl = 17{\cdot}75$; $I = 63{\cdot}18$; $Br = 40$; $F = 9{\cdot}35$. Metallic protoxides are represented by the formula MO: *e. g.* potash = KO; black oxide of copper = CuO.

3. The system of Gerhardt is based, like that of Berzelius, on the hypothesis that all simple gases contain equal numbers of atoms in equal volumes, but carrying out that system more consistently. The formula of water in Gerhardt's system is H_2O, as in that of Berzelius. Moreover, as the vapour-density of mercury is to that of oxygen as 6976 : 1106 (p. 130), and mercuric oxide contains 8 parts by weight of oxygen to 100 parts of mercury, it follows that the proportions by volume of mercury-vapour and oxygen which compose this oxide must be 2 vol. mercury to 1 vol. oxygen: for $2 \times 6976 : 1106 = 100 : 8$ (nearly). Hence mercuric oxide is Hg_2O; and from the analogy of cupric oxide, ferrous oxide, potash, soda, &c., with mercuric oxide, it follows that these oxides must be Cu_2O, Fe_2O, K_2O, Na_2O, &c.; or, generally, the formula of a protoxide is M_2O, analogous to that of water, H_2O.

If $O = 8$, the atomic weights of sulphur, selenium, tellurium, and carbon are the same in Gerhardt's system as in that adopted in the present work, but those of all the other elements have only half the usual values:—$H = 0{\cdot}5$, $Cl = 17{\cdot}75$, $K = 19{\cdot}5$, &c. Or, what is more convenient, assuming $H = 1$, the atomic weights of O, Se, Te, and C will be doubled, while those of all the other elements will remain the same.*

In the following explanations and applications of Gerhardt's system, these double atomic weights of oxygen, &c., will, to avoid confusion, be denoted by letters with bars through the middle: thus, $\Theta = 16$, $\text{Ꞩ} = 32$, $\text{Ȼ} = 12$.

The following table presents a comparative view of the formulæ of some of the most important chemical compounds in the ordinary notation, and in that of Gerhardt.

	Ordinary System.	Gerhardt's System.
Water	HO	$H_2\Theta$
Peroxide of hydrogen	HO_2	$H\Theta$
Hydrosulphuric acid	HS	$H_2\text{Ꞩ}$
Sulphuric acid (anhydrous)	SO_3	$\text{Ꞩ}\Theta_3$
" " (hydrated)	SHO_4	$\text{Ꞩ}H_2\Theta_4$
Hydrochloric acid	HCl	HCl
Hypochlorous acid (anhydrous)	ClO	$Cl_2\Theta$
" " (hydrated)	$ClHO_2$	$ClH\Theta$
Carbonic oxide	CO	$\text{Ȼ}\Theta$
Carbonic acid (anhydrous)	CO_2	$\text{Ȼ}\Theta_2$
Nitric acid (anhydrous)	NO_5	$N_2\Theta_5$
" " (hydrated)	NHO_6	$NH\Theta_3$
Phosphoric acid (anhydrous)	PO_5	$P_2\Theta_5$
" " (hydrated)	PH_3O_8	$PH_3\Theta_4$
Protoxides (anhydrous)	MO	$M_2\Theta$
" (hydrated)	$\left\{ \begin{array}{c} MHO_2 \\ \text{or } MO.HO \end{array} \right\}$	$MH\Theta$
Sesquioxides (anhydrous)	M_2O_3	$M_4\Theta_3$
Sulphate of potash (neutral)	SKO_4	$\text{Ꞩ}K_2\Theta_4$
" " (acid)	S_2KHO_8	$\text{Ꞩ}KH\Theta_4$
Nitrate of potash	NKO_6	$NK\Theta_3$
Alum (anhydrous)	$S_4KAl_2O_{16}$	$\text{Ꞩ}_2KAl_2\Theta$
Hydrocyanic acid	C_2NH	$\text{Ȼ}NH$
Cyanic acid	C_2NHO_2	$\text{Ȼ}NH\Theta$
Cyanate of soda	C_2NNaO_2	$\text{Ȼ}NNa\Theta$
Hydrosulphocyanic acid	C_2NHS_2	$\text{Ȼ}NH\text{Ꞩ}$
Sulphocyanide of silver	C_2NAgS_2	$\text{Ȼ}NAg\text{Ꞩ}$
Alcohol	$C_4H_6O_2$	$\text{Ȼ}_2H_6\Theta$
Ether	C_4H_5O	$\text{Ȼ}_4H_{10}\Theta$
Acetic acid (hydrated)	$C_4H_4O_4$	$\text{Ȼ}_2H_4\Theta_2$
" " (anhydrous)	$C_4H_3O_3$	$\text{Ȼ}_4H_6\Theta_3$
Benzoic acid (hydrated)	$C_{14}H_6O_4$	$\text{Ȼ}_7H_6\Theta_2$
" " (anhydrous)	$C_{14}H_5O_3$	$\text{Ȼ}_{14}H_{10}\Theta_3$
Benzoate of potash	$C_{14}H_5KO_4$	$\text{Ȼ}_7H_5K\Theta_2$
Oxalic acid	$C_4H_2O_8$	$\text{Ȼ}_2H_2\Theta_4$

These two systems of notation possess in common the advantage of representing the metallic protoxides by formulæ analogous to that of water, whereas in the system of Berzelius, this analogy is lost, water being represented by $H_2\Theta$, and the protoxides of the metals by $M\Theta$. But the representation of water by $HH\Theta$, as in Gerhardt's system, possesses the additional advantage of corresponding with the important fact, that it is possible to replace either the half or the whole of the hydrogen in water by a metal. Thus potassium thrown into water displaces half the hydrogen, and forms hydrate of potash, $HK\Theta$; and when this compound, in

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* Gmelin, in his Handbook (Translation, vol. vii. p. 27), objects to Gerhardt's atomic weights, that they do not correspond with the equivalent numbers; but this, as already shown (p. 686), must necessarily be the case with all systems of atomic weights or combining numbers, inasmuch as a body may have several equivalents, but can have only one atomic weight.

the solid state, is heated with an additional quantity of potassium, the remaining half of the hydrogen is displaced, and anhydrous potash, $KK\Theta$, is formed. On the contrary, when potassium acts on hydrochloric acid, HCl, it displaces the whole of the hydrogen, and forms chloride of potassium, KCl. This is an important difference, which is easily understood on the supposition that water contains two atoms and hydrochloric acid only one atom of hydrogen; whereas, if these two compounds are represented by the analogous formulæ, HO and HCl, the cause of the difference of action is by no means apparent.

Assuming as the unit of vapour-volume the space occupied by 1 gramme of hydrogen (or by 16 grammes of oxygen, 14 of nitrogen, 35·5 of chlorine, &c.), and calculating by formulæ analogous to those in third column of the preceding table, the weights of the compound atoms or molecules of those compounds which are capable of assuming the gaseous form, it will be found that they correspond to 2 volumes of vapour. Thus, for hydrochloric acid: $H + Cl = 1 + 35{\cdot}5 = 36{\cdot}5$; and as the density of hydrochloric acid gas is 18·25 times that of hydrogen (see Table I. p. 131), it follows that the number 36·5 represents the weight of 2 volumes of vapour. Similarly, for water: $H_2\Theta = 2 + 16 = 18$, which is also the weight of 2 volumes of vapour, the specific gravity of aqueous vapour compared with hydrogen as the unit being 9. Alcohol $= \text{Ȼ}_2H_6\Theta = 24 + 6 + 16 = 46$: and the specific gravity of alcohol vapour $(H = 1)$ is 23. Ether $= \text{Ȼ}_4H_{10}\Theta = 48 + 10 + 16 = 74$, which is twice 37, the weight of a unit-volume of ether-vapour.

In the formulæ of the second column, this uniformity of vapour-volume is not observed. Some of them, as those of water HO, ether C_4H_5O, anhydrous acetic acid $C_4H_3O_3$, and hydrated sulphuric acid SHO_4, represent 1 volume of vapour, when referred to the unit above-mentioned, viz. the space occupied by 1 gramme of hydrogen, or 2 volumes, if compared with the volume of half a gramme of hydrogen, or 8 grammes of oxygen; while the rest, for example, hydrochloric acid, HCl, and hydrated acetic acid, $C_4H_4O_4$, represent 2 volumes or 4 volumes of vapour, according to the unit adopted. (See the table on pp. 130–136.) To bring all these formulæ to the same standard of vapour-volume, it is necessary, therefore, to double those first mentioned, thus: water $= H_2O_2$; ether, $C_8H_{10}O_2$; anhydrous acetic acid, $C_8H_6O_6$; hydrated sulphuric acid, $S_2H_2O_8$, &c.; and if the corresponding change be made in the formulæ of the analogous compounds, which are not known to exist in the gaseous state, *e. g.* anhydrous metallic protoxides, M_2O_2; neutral sulphate of potash, $S_2K_2O_8$, &c., it will be found that Gerhardt's formulæ may, in all cases, be converted into those of the ordinary notation, by doubling the number of atoms of carbon, oxygen, sulphur, selenium, and tellurium.*

There is yet one class of bodies whose atomic weights represent, not two, but one volume of vapour, viz. the elementary bodies. To reduce these bodies to the same standard, it is necessary to assume that each molecule of an elementary body in the free state consists of two elementary atoms, *e. g.* hydrogen, HH; chlorine, $ClCl$.

This hypothesis is justified by numerous considerations. First: It accords with the polar view of the constitution of bodies suggested by the phenomena of electrolysis (p. 189). Secondly: It is justified by certain relations of boiling point and vapour-density, to be considered hereafter. Thirdly: There are numerous instances of chemical action in which two atoms of an elementary body unite together at the moment of chemical change, just like heterogeneous atoms. Thus,

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* Gerhardt applied the term *unitary* to his system of notation, because it is based on the reduction of all formulæ to one common standard, the formulæ being derived, one from the other, by substitution. The ordinary system, being founded rather on the formation of compounds in successive binary groups (*e. g.* potash $= KO$; sulphuric acid $= SO_3$; sulphate of potash $= KO.SO_3$), is called the *Dualistic system.*

when the hydride of copper, Cu_2H, is decomposed by hydrochloric acid, cuprous chloride is formed, and a quantity of hydrogen evolved equal to twice that which is contained in the hydride itself:—

$$Cu_2H + HCl = Cu_2Cl + HH.$$

This action is analogous to that of hydrochloric acid on cuprous oxide:—

$$Cu_4\Theta + 2HCl = 2Cu_2Cl + H_2\Theta.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen; in the former, with hydrogen. When solutions of sulphurous and hydrosulphuric acids are mixed, the whole of the sulphur is precipitated:—

$$\text{Ꞩ}\Theta_2 + 2H_2\text{Ꞩ} = 2H_2\Theta + \text{Ꞩ}.\text{Ꞩ}_2,$$

the action being similar to that of sulphurous acid on hydroselenic acid:—

$$\text{Ꞩ}\Theta_2 + 2H_2\text{Ꞩ}e = 2H_2\Theta + \text{Ꞩ}.\text{Ꞩ}e_2.$$

In the one case, a sulphide of selenium is formed; in the other a sulphide of sulphur. The precipitation of iodine which takes place on mixing hydriodic with iodic acid, affords a similar instance of the combination of homogeneous atoms. The reduction of certain metallic oxides by peroxide of hydrogen, is another striking example of this kind of action. When oxide of silver is thrown into this liquid, water is formed; the silver is reduced to the metallic state; and a quantity of oxygen is evolved equal to twice that which is contained in the oxide of silver. It appears, indeed, as if atoms could not exist in a state of isolation. An atom of an elementary body must unite, either with an atom of another element, or with one of its own kind.

The same tendency of homogeneous atoms to combine together is exhibited by certain groups of atoms called compound radicals, which behave in most respects like elementary substances, and pass as entire groups from one state of combination to another. Thus there is a series of hydrocarbons called the *alcohol-radicals* (p. 697), *e.g.* methyl, $\text{Ꞓ}H_3$; ethyl, Ꞓ_2H_5, which may be regarded as compound metals, capable of taking the place of hydrogen in combination with chlorine, iodine, oxygen, &c., just as simple metals do. Now when zinc-ethyl, Ꞓ_2H_5Zn, and iodide of methyl, $\text{Ꞓ}H_3I$, are heated together, double decomposition takes place, the products being iodide of zinc, and methyl-ethyl:—

$$\text{Ꞓ}_2H_5.Zn + \text{Ꞓ}H_3I = ZnI + (\text{Ꞓ}_2H_5).(\text{Ꞓ}H_3).$$

And when zinc-ethyl is heated with iodide of ethyl, a similar action takes place, but attended with formation of free ethyl:—

$$\text{Ꞓ}_2H_5.Zn + \text{Ꞓ}_2H_5I = ZnI + (\text{Ꞓ}_2H_5).(\text{Ꞓ}_2H_5).$$

Moreover, the boiling points and vapour-densities of these radicals are related to each other and to those of the compound radicals, methyl-ethyl, butyl-amyl, &c., in a manner which can only be explained by supposing the radicals in the free state to consist of double atoms. This will be seen from the following Table:—

	Sp. gr. at 0° C.	Vapour-density.	Boiling-point.
Ethyl-butyl ...... Ꞓ_2H_5 ... Ꞓ_4H_9	0·7011	3·053	62° C.
Ethyl-amyl ...... Ꞓ_2H_5 ... Ꞓ_5H_{11}	0·7069	3·522	88
Butyl .... Ꞓ_4H_9 ... Ꞓ_4H_9	0·7057	4·070	106
Butyl-amyl ...... Ꞓ_4H_9 ... Ꞓ_5H_{11}	0·7247	4·465	132
Amyl .... Ꞓ_5H_{11} ... Ꞓ_5H_{11}	0·7413	4·956	158
Butyl-caproyl ... Ꞓ_4H_9 ... Ꞓ_6H_{13}	?	4·917	155
Caproyl .... Ꞓ_6H_{13} ... Ꞓ_6H_{13}	0·7561	5·983	202

The regular gradation of these densities and boiling points plainly shows that the proper places of butyl, amyl, and caproyl in the series, are those which they occupy in the table, and consequently that their atomic weights in the free state are double of those which appertain to them in combination: *e. g.*, amyl in combination $= \text{Ꞓ}_5\mathrm{H}_{11} = 71$; free amyl $= (\text{Ꞓ}_5\mathrm{H}_{11})_2 = 142$.

Fourthly: Elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon potash forms two compounds, chloride of potassium and hypochlorite of potash:—

$$\mathrm{KK\Theta} + \mathrm{ClCl} = \mathrm{ClK} + \mathrm{ClK\Theta};$$

just as chloride of cyanogen would form chloride of potassium and cyanate of potash. The quantity of chlorine which acts upon an atom of potash, is not 1 at. = 35·5, but 2 at. = 70. Similarly, when metallic sulphides oxidize in the air, both the metal and the sulphur enter into combination with oxygen. Sulphur acting upon potash forms a sulphide and a hyposulphite. Lastly, when zinc-ethyl is exposed to the action of chlorine, iodine, &c., these elements unite separately with the zinc and with the ethyl, thus:—

$$\text{Ꞓ}_2\mathrm{H}_5\mathrm{Zn} + \mathrm{ClCl} = \text{Ꞓ}_2\mathrm{H}_5\mathrm{Cl} + \mathrm{ZnCl}.$$

Double Decomposition regarded as the Type of Chemical Action in general.— Double decomposition is generally understood as an action taking place between four elements or groups of elements; but since it appears that homogeneous atoms may exhibit towards one another the same chemical relations as atoms of different bodies, it follows that the same kind of action may be supposed to take place when less than four bodies are concerned. The extension of this view of chemical action to cases in which three elements or groups of elements come into play, is sufficiently illustrated by the examples just given. But we may proceed still further in the same direction, and regard as double decompositions those reactions which are commonly viewed as the simple combination or separation of two elements, or as the substitution of one element for another. Thus, when potassium burns in chlorine gas, the reaction may be supposed to take place between two atoms of chlorine and two atoms of potassium:—

$$\mathrm{KK} + \mathrm{ClCl} = \mathrm{KCl} + \mathrm{KCl}.$$

Again, the decomposition of cyanide of mercury by heat may be represented thus:—

$$\mathrm{CyHg}\,.\,\mathrm{CyHg} = \mathrm{CyCy} + \mathrm{HgHg}.$$

The simple replacement of one element by another may also be regarded as a double decomposition, by supposing the formation of an intermediate compound to take place. Thus, the action of zinc upon hydrochloric acid may be supposed to consist of two stages:—

$$\mathrm{ZnZn} + \mathrm{HCl} = \mathrm{ZnH} + \mathrm{ZnCl},$$

and

$$\mathrm{ZnH} + \mathrm{HCl} = \mathrm{ZnCl} + \mathrm{HH}.$$

It is true that the formation of the intermediate compound, the hydride of zinc, cannot be actually demonstrated in this case, because it is decomposed as fast as it is formed; but in other cases the two stages of the action can be distinctly traced. Thus, it is well known that hydrochloric acid does not dissolve copper; but an alloy of zinc and copper, $\mathrm{Cu_2Zn}$, dissolves in it readily, with evolution of hydrogen. Here it may be supposed that the first products are chloride of zinc and hydride of copper, a known compound:—

$$Cu_2Zn + HCl = Cu_2H + ZnCl;$$

and that the hydride is afterwards acted upon by the acid in the manner already explained. Again, when zinc and iodide of ethyl are heated together in a sealed tube, iodide of zinc and zinc-ethyl are obtained, thus: —

$$ZnZn + (Ꞓ_2H_5) . I = ZnI + Zn\,(Ꞓ_2H_5);$$

and the zinc-ethyl, when heated with excess of iodide of ethyl, yields iodide of zinc and free ethyl: —

$$Zn\,(Ꞓ_2H_5) + Ꞓ_2H_5) . I = ZnI + (Ꞓ_2H_5)\,(Ꞓ_2H_5).$$

In this manner, all chemical reactions may be reduced to one type, viz., a mutual interchange of atoms between two binary groups.

TYPES AND RADICALS. — RATIONAL FORMULÆ.

The rational formula of a compound is inferred from its modes of formation and decomposition. When cyanide of sodium is mixed with nitrate of silver, an interchange of elements takes place, resulting in the formation of nitrate of soda and cyanide of silver: —

$$ꞒN . Na + NƟ_3 . Ag = ꞒN . Ag + NƟ_3 . Na.$$

Here the group, or radical $NƟ_3$ passes from the silver to the sodium, and in a similar manner it may be transferred to potassium, barium, copper, &c. Hence it may be inferred that the nitrates consist of $NƟ_3$ associated with a metal. Similarly, $ꞒN$, may be regarded as the radical of the cyanides; $ꞨƟ_4$ of the sulphates, &c. When alcohol, $Ꞓ_2H_6Ɵ$, is treated with potassium, one-sixth of the hydrogen is evolved, and the compound $Ꞓ_2H_5KƟ$ is formed. Again,—alcohol treated with chloride, bromide, and iodide of phosphorus, yields the compounds, $Ꞓ_2H_5Cl$, $Ꞓ_2H_5Br$, and $Ꞓ_2H_5I$; and when the compound $Ꞓ_2H_5KƟ$ is treated with $Ꞓ_2H_5I$, iodide of potassium and ether are formed: —

$$Ꞓ_2H_5I + \left.\begin{matrix}Ꞓ_2H_5\\K\end{matrix}\right\}Ɵ = KI + \left.\begin{matrix}Ꞓ_2H_5\\Ꞓ_2H_5\end{matrix}\right\}Ɵ.$$

From these and other reactions, alcohol and its derivatives are supposed to contain the radical ethyl, $Ꞓ_2H_5$, alcohol being its hydrated oxide, $\left.\begin{matrix}Ꞓ_2H_5\\H\end{matrix}\right\}Ɵ$, analogous to hydrate of potash, $\left.\begin{matrix}K\\H\end{matrix}\right\}Ɵ$, and ether its anhydrous oxide, $\left.\begin{matrix}Ꞓ_2H_5\\Ꞓ_2H_5\end{matrix}\right\}Ɵ$, analogous to $\left.\begin{matrix}K\\K\end{matrix}\right\}Ɵ$.

It must be especially observed, however, that the reason for admitting the existence of ethyl as a radical in the alcohol compounds, is that this supposition affords the readiest explanation of certain reactions. Other reactions may point to a different conclusion. Thus, since alcohol heated to a high temperature with strong sulphuric acid is resolved into olefiant gas and water, it may be regarded as a hydrate of olefiant gas, $Ꞓ_2H_4 . H_2Ɵ$. Again, — certain sulphates, when heated to redness, give off anhydrous sulphuric acid; and sulphate of baryta may be formed by the direct combination of the same anhydrous acid with anhydrous baryta. Such reactions might lead to the conclusion that oxygen-salts are compounds of anhydrous metallic oxides with anhydrous acids, rather than of metals with salt-radicals, which is, in fact, the ordinary view. Similarly, ammoniacal salts are regarded as compounds of NH_3 with hydrated acids, or of NH_4 with acid radicals, according to the actions specially under consideration.

It appears, then, that the same compound may have several rational formulæ. This of course implies that the formula is an expression, not of the constitution of the body in a state of rest, but of the manner in which the atoms are supposed to arrange themselves when subjected to certain influences. It is no longer the question what the absolute constitution of a substance may be, but of how many forms of constitution the substance fulfils the conditions. For in chemical substances, as in the objects of a branch of natural history, any one individual exhibits more or less distinctly the features of every other.

The greater the number of elementary atoms entering into the constitution of a compound, the more numerous will be the possible arrangements of those atoms, and the greater, therefore, the number of rational formulæ which may be assigned to the compound. Practically, however, it is found that a small number of rational formulæ—seldom more than two or three—suffices for each compound; and moreover, that the formulæ of all bodies whatever may be reduced to a small number of general types. Of these, Gerhardt adopts four, viz.: —

Water, $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$, from which are derived the oxides, sulphides, selenides, and tellurides.

Hydrochloric acid, HCl, the type of the chlorides, bromides, iodides, fluorides, and cyanides.

Ammonia, $N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$, the type of the nitrides, phosphides, arsenides, &c.

Hydrogen, HH, the type of the elementary bodies, compound radicals, hydrides of metals and radicals, &c.

These typical formulæ all correspond to 2 volumes of vapour.

The formulæ of the several compounds included under each of these types are obtained by replacing one or more of the elementary atoms contained in them by another radical, simple or compound. The derivative compound is called *primary*, *secondary*, or *tertiary*, according to the number of atoms of hydrogen in the type which are thus replaced. For example, the hydrated metallic oxides, which are formed from the type water by the substitution of 1 at. of a metal for 1 at. hydrogen, are primary oxides; *e. g.* hydrate of potash, $\left.\begin{matrix}H\\K\end{matrix}\right\}\Theta$; the anhydrous oxides, in which both atoms of hydrogen are similarly replaced, as in anhydrous potash, $\left.\begin{matrix}K\\K\end{matrix}\right\}\Theta$, are secondary oxides. The replacement of 1 at. H in ammonia by ethyl, Ꞓ_2H_5, forms a primary nitride, viz., ethylamine, $N(\text{Ꞓ}_2H_5)H_2$; similarly, biethylamine, $N(\text{Ꞓ}_2H_5)_2H$, is a secondary nitride; and triethylamine, $N(C_2H_5)_3$, a tertiary nitride.

Equivalent Values of Radicals.—A radical is *monatomic*, *biatomic*, *triatomic*, &c., according as its atom or molecule is equivalent to one, two, three, &c., atoms of hydrogen. Potassium and ethyl are monatomic radicals. *Sulphuryl*, $S\Theta_2$, is a biatomic radical, and by replacing 2 at. H in two molecules of water, $\left.\begin{matrix}H^2\\H_2\end{matrix}\right\}\Theta_2$, forms hydrated sulphuric acid, $\left.\begin{matrix}S_2\Theta\\H_2\end{matrix}\right\}\Theta$. *Phosphoryl*, $P\Theta$, is a triatomic radical, and by replacing 3 atoms of hydrogen in three molecules of water, $\left.\begin{matrix}H^3\\H_3\end{matrix}\right\}\Theta_3$, forms the ordinary hydrate of phosphoric acid, $PH_3\Theta_4 = \left.\begin{matrix}P\Theta\\H_3\end{matrix}\right\}\Theta_3$.

When a metal forms two classes of salts, its atom has a different equivalent value in each. Thus, in the platinous compounds, Pt (=98) is monatomic; in the platinic salts, it is biatomic: thus, platinic chloride $= \mathrm{Pt}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.$. In the ferrous compounds, Fe ($= 28$) is monatomic; in the ferric compounds, it is sesquiatomic, Fe_2, being equivalent to H_3, or $Fe\frac{2}{3}$ to H: thus, ferric oxide $= \left.\begin{matrix}Fe_2\\ Fe_2\end{matrix}\right\}\Theta_3$. In the mercuric compounds, Hg ($= 100$) is monatomic; in the mercurous compounds, it is semi-atomic; the double atom, Hg_2 ($= 200$), being the equivalent of 1 atom of hydrogen. In arsenious acid, $As_2\Theta_3$, which is derived from 3 molecules of water, As_2, is equivalent to H_6, and therefore As to H_3; but in arsenic acid, $As_2\Theta_5$, derived from 5 molecules of water, As is equivalent to H_5.*

Since a compound may have several rational formulæ, or, in other words, may be represented as containing different radicals, it is necessary to determine the relation which exists between the equivalents of such radicals. This relation is determined by the following general law: — *Every equivalent of hydrogen added to a radical diminishes by unity the equivalent value of the entire radical; and every equivalent of hydrogen subtracted from a radical increases by unity the total equivalent value of the entire radical.* Thus, nitric acid may be represented by the three following formula:—

$$\left.\begin{matrix}N\Theta^2\\ H\end{matrix}\right\}\Theta, \qquad \left.\begin{matrix}N\Theta\\ H\end{matrix}\right\}\Theta_2, \qquad \left.\begin{matrix}N\\ H\end{matrix}\right\}\Theta_3.$$

In the first of these formulæ, which represents nitric acid as formed from one molecule of water, $H_2\Theta$, the radical *nitryl*, $N\Theta_2$, is equivalent to 1 atom of hydrogen; in the second, which is formed from 2 molecules of water, $H_4\Theta_2$, the radical *azotyl*, $N\Theta$, formed from nitryl by abstraction of Θ, the equivalent of H_2, takes the place of 3 atoms of hydrogen; and in the third, which is formed from 3 molecules of water, $H_6\Theta_3$, the radical *nitricum*, N, formed from nitryl by abstraction of Θ_2, the equivalent of H_4, takes the place of 5 atoms of hydrogen. Again, uranic oxide may be represented either as $\left.\begin{matrix}U_2\\ U_2\end{matrix}\right\}\Theta_3$, or as $\left.\begin{matrix}U_2\Theta\\ U_2\Theta\end{matrix}\right\}\Theta$. The first of these formulæ represents three molecules of water, $H_6\Theta_3$, and contains the radical $U_2 = H_3$; the second represents one molecule of water, and contains the radical *uranyl*, $U_2\Theta$, equivalent to H; and accordingly, $U_2 - \Theta$, is equivalent to $H_3 - H_2 = H$. Another example of the general law above stated is afforded by the radicals of the monatomic, biatomic, and triatomic alcohols (p. 697).

Conjugate Radicals. — Any compound radical may be regarded as a compound of two or more simpler radicals. Thus, ethyl, Ꞓ_2H_5, may be represented as $\text{Ꞓ}H_2 + CH_3$, or as $\text{Ꞓ}_2H_3 + H_2$; acetyl, $\text{Ꞓ}_2H_3\Theta$, the radical of acetic acid may be regarded as $\text{Ꞓ}\Theta + \text{Ꞓ}H_3$, or as $\text{Ꞓ}_2H_3 + \Theta$, &c. Radicals viewed in this manner are said to be *conjugated*. A radical may be conjugated either by addition, as in the preceding examples, or by substitution of another radical for one or more atoms

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* If the notion of equivalents be strictly adhered to, independently of the atomic theory, the formulæ of bisalts and sesquisalts may be dispensed with, and the different classes of salts of the same metal regarded as containing different radicals: thus the mercurous salts may be regarded as salts of *mercurosum*, $Hg = 200$; the mercuric salts as containing *mercuricum*, $hg = 100$: thus—

Mercurous chloride or chloride of mercurosum	$HgCl = 200 + 35{\cdot}5$
Mercuric chloride or chloride of mercuricum	$hgCl = 100 + 35{\cdot}5$
Ferrous chloride or chloride of ferrosum	$FeCl = 28 + 35{\cdot}5$
Ferric chloride or chloride of ferricum	$feCl = 18\frac{2}{3} + 35{\cdot}5$

This mode of representation might be made consistent with the atomic theory, by supposing that the ultimate atom of iron weighs $9\frac{1}{3}$; that a double atom of iron constitutes ferricum $= 18\frac{2}{3}$; and a triple atom, ferrosum, $= 28$; similarly, the atom of mercury weighing 100, a double atom constitutes mercurosum. In organic compounds, such relations between radicals are actually observed: thus, ethylene, $\text{Ꞓ}_2H_4 = 2 \times \text{Ꞓ}H_2$; propylene, $\text{Ꞓ}_3H_6 = 3 \times \text{Ꞓ}H_2$; butylene, $\text{Ꞓ}_4H_8 = 4 \times \text{Ꞓ}H_2$, &c.

of hydrogen; *e. g.*, from benzoyl, $Ꞓ_7H_5O$, is formed nitro-benzoyl, $Ꞓ_7H_4(NƟ_2)Ɵ$, by substitution of a molecule of nitryl, $NƟ_2$, for 1 at. H. Similarly, from acetyl, $Ꞓ_2H_3Ɵ$, are formed monochloracetyl, $Ꞓ_2(H_2Cl)Ɵ$, and terchloracetyl, $Ꞓ_2Cl_3Ɵ$.

An important class of conjugate radicals consists of those which are formed of certain metals—arsenic, antimony, tin, bismuth, &c.,—associated with the alcohol-radicals. For example: cacodyl, or arsen-bimethyl, $As(ꞒH_3)_2$; stibethyl, $Sb(Ꞓ_2H_5)_3$; arsenethylium, $As(Ꞓ_2H_5)_4$; stannethyl, $Sn.Ꞓ_2H_5$. The same radicals may be regarded as conjugated by substitution: *e. g.*, arsenethyl, $As(Ꞓ_2H_5)_3$, as formed from ammonia, NH_3, the 3 at. H being replaced by ethyl, and the nitrogen by arsenic. In like manner, arsenethylium, $As(Ꞓ_2H_5)_4$, may be derived from ammonium, NH_4.

The equivalent in hydrogen of a conjugate radical may be determined by the two following rules, deduced from the general law given at page 694:—

1. *The equivalent in hydrogen of a radical conjugated by addition is equal to the difference of the equivalents of the constituent radicals.* Thus, acetyl $(Ꞓ_2H_3)Ɵ$, which is equivalent to H, is composed of acetosyl, $Ꞓ_2H_3$, eq. to H, and Ɵ eq. to H_2; arsenethyl. $As(Ꞓ_2H_5)_3$, which is equivalent to H_2, is composed of As(arsenicum), eq. to H_5,* and $(Ꞓ_2H_5)_3$, eq. to H_3; cacodyl, $As(ꞒH_3)_2$, which is equivalent to H, is composed of As(arsenosum), eq. to H_3, and $(ꞒH_3)_2$, eq. to H_2.

2. *The equivalent in hydrogen of a radical conjugated by substitution is equal to the difference between the sum of the equivalents of the constituent radicals and the equivalent of the hydrogen replaced.* For example, —acetyl $Ꞓ_2H_3Ɵ$, which is equivalent to H, may be regarded as $Ꞓ_2H_5 + Ɵ$ (eq. to $H + H_2$) *minus* H_2.

CLASSIFICATION OF CHEMICAL COMPOUNDS.

Bodies may be classified in two ways. 1. According to their origin, as when the acids, salts, oxides, &c., of copper are made to form one group; those of chromium another, those of ethyl a third, &c. 2. According to their chemical functions, independenly of origin; the acids forming one group, the bases a second, the alcohols a third, the ethers a fourth, &c. The former mode of classification is best adapted to the detailed description of compounds; the latter for giving a general view of their mutual relations.

The following table exhibits Gerhardt's system of classification by types, or according to chemical functions: —

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* Oxide of arsenethyl is $As(Ꞓ_2H_5)_3Ɵ$ or $As_2(C_2H_5)_6Ɵ_2$: now as $(Ꞓ_2H_5)_2$ is equivalent to Ɵ, this last formula may be derived from that of arsenic acid, $As_2Ɵ_5$ or $As_2Ɵ_3.Ɵ_2$ by the substitution of $(Ꞓ_2H_5)_6$ for $Ɵ_3$; hence As has in oxide of arsenethyl the same equivalent value that it has in arsenic acid: that is to say, it is equivalent to H_5. On the other hand, oxide of cacodyl is $As_2(ꞒH_3)_4Ɵ$; which has the same equivalent value as $As_2.Ɵ_2Ɵ$, or $As_2Ɵ_3$, which is the formula of arsenious acid. Hence the radical As in cacodyl has the same value as in arsenious acid, viz., equivalent to H_3.

CLASSIFICATION OF BODIES ACCORDING TO THEIR CHEMICAL FUNCTIONS.

	WATER TYPE. $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$.		HYDROCHLORIC-ACID TYPE. HCl.		AMMONIA TYPE, $N\left\{\begin{matrix}H\\H.\\H\end{matrix}\right.$	HYDROGEN TYPE, HH.
	OXIDES.	SULPHIDES. (Selenides, Tellurides).	CHLORIDES. (Bromides, Iodides, Fluorides).	CYANIDES.	NITRIDES. (Phosphides).	METALS. Metalloïds.
Derivatives with Positive Radicals.	**Bases proper.** 1. *Primary* or *hydrated bases* (hydrate of potash $^{H}_{K}\Theta$, hydrate of arsenethylium). 2. *Secondary* or *anhydrous bases* (oxide of potassium).	**Basic Sulphides.** 1. *Primary* or *hydrosulphates* (hydrosulphate of potassium). 2. *Secondary* or *metallic sulphides* (sulphide of potassium).	**Basic Chlorides.** *Metallic chlorides* (chloride of potatsium).	**Basic Cyanides.** *Metallic cyanides* (cyanide of potassium, ferrocyanide of potassium).	**Basic Nitrides.** 1. *Primary* (amide of potassium). 2. *Secondary.* 3. *Tertiary* (nitride of potassium).	**Basic Metals.** 1. *Primary* or *metallic hydrides* (hydride of copper). 2. *Secondary* or *metals proper* (potassium, stibethyl, tetrethylium).
	Alcohols or Hydrocarburetted Bases. 1. *Primary* or *alcohols proper* (vinic alcohol, hydrate of phenyl, glycol, glycerine). 2. *Secondary alcohols* or *ethers* (oxide of ethyl).	**Alcoholic Sulphides.** 1. *Primary* or *mercaptans* (hydrosulphate of ethyl). 2. *Secondary* or *hydrosulphuric ethers* (sulphide of ethyl).	**Alcoholic Chlorides.** *Hydrochloric ethers* (chloride of ethyl).	**Alcoholic Cyanides.** *Hydrocyanic ethers* or *nitriles* (acetonitrile, hydrocyanic acid).	**Alcoholic Nitrides.** 1. *Primary* (ethylamine). 2. *Secondary* (biethylamine). 3. *Tertiary* (triethylamine).	**Alcoholic Metals.** 1. *Primary* or *alcoholic hydrides* (marsh-gas, benzin). 2. *Secondary*: the so-called *alcohol-radicals* (ethyl, amyl, phenyl).
	Aldehydes. 1. *Primary* (acetic aldehyde, bitter almond oil). 2. *Secondary.*	**Aldehydic Sulphides.** 1. *Primary* (sulphobenzol). 2. *Secondary.*	**Aldehydic Chlorides.** Chloride of aldehydene.	**Aldehydic Cyanides.**	**Aldehydic Nitrides.** 1. *Primary.* 2. *Secondary.* 3. *Tertiary.*	**Aldehydic Metals.** 1. *Primary* or *aldehydic hydrides* (olefiant gas). 2. *Secondary.*
Derivatives with Negative Radicals.	**Acids.** 1. *Primary* or *hydrated acids* (sulphuric, acetic, cyanic acids). 2. *Secondary* or *anhydrous acids.*	**Acid Sulphides.** 1. *Primary* (hydrosulphocyanic acid). 2. *Secondary* (sulphide of benzoyl).	**Acid Chlorides.** Chloride of acetyl, oxychloride of phosphorus, chloride of cyanogen, free chlorine.	**Acid Cyanides.** Cyanide of benzoyl, free cyanogen.	**Acid Nitrides.** 1. *Primary* (benzamide, cyanamide, succinamide). 2. *Secondary* (succinimide, benzoyl-phenylamide). 3. *Tertiary* (bibenzoyl-salicylamide, boramide, free nitrogen).	**Acid Metals.** 1. *Primary* or *acid hydrides* (hydride of benzoyl, hydrochloric acid, hydrocyanic acid). 2. *Secondary* or *metalloids* (benzoyl, chlorine, cyanogen).
Intermediate Derivatives.	**Oxygen-salts.** Sulphates, nitrates, cyanates.	**Sulphur-salts.** Sulphocyanides, sulphantimoniates,			**Amidogen-salts.** Benzamidate of mercury.	Here might be placed many compounds already included in the preceding classes: *e.g*, the cyanides of ethyl, &c., containing the radical of cyanic acid and an alcohol-radical.
	Compound Ethers. Sulphate, cyanate, oxalate of ethyl, glycerides, stearin, &c.	**Comp'nd Sulphur-ethers.** Thiacetate of ethyl, sulphocyanide of ethyl.			**Alcalamides.** Oxanilide, ethylacetamide.	
	Compound Aldehydes.	**Com. Sulphur-aldehydes.**				

WATER-TYPE.

Positive Oxides.—*A. Bases proper, or Metallic Oxides.*—These compounds are formed by the substitution of a metallic radical, simple or compound, for the hydrogen, in one, two, or three molecules of water:—

a. Monatomic.—Hydrate of potash, $\left.\begin{matrix}K\\H\end{matrix}\right\}\Theta$; anhydrous potash or oxide of potassium, $\left.\begin{matrix}K\\K\end{matrix}\right\}\Theta$;—cupric hydrate, $\left.\begin{matrix}Cu\\H\end{matrix}\right\}\Theta$;—cupric oxide, $\left.\begin{matrix}Cu\\Cu\end{matrix}\right\}\Theta$;—hydrate of ammonium, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}\Theta$;—hydrate of tetramercurammonium, $\left.\begin{matrix}NHg_4\\H\end{matrix}\right\}\Theta$;—hydrate of tetrethylium, $\left.\begin{matrix}N(\bar{C}_2H_5)_4\\H\end{matrix}\right\}\Theta$;—oxide of cacodyl, $\left.\begin{matrix}As(\bar{C}H_3)_2\\As(CH_3)_2\end{matrix}\right\}\Theta$;—oxide of arsenethylium, $\left.\begin{matrix}As(\bar{C}_2H_5)_4\\As(\bar{C}_2H_5)_4\end{matrix}\right\}\Theta$.

β. Biatomic.—Platinic hydrate, $\left.\begin{matrix}Pt\\H_2\end{matrix}\right\}\Theta_2$; platinic oxide, $\left.\begin{matrix}Pt\\Pt\end{matrix}\right\}\Theta_2$; oxide of stibethyl, $\left.\begin{matrix}Sb(\bar{C}_2H_5)_3\\Sb(C_2H_5)_3\end{matrix}\right\}\Theta_2$.*

γ. Triatomic.—Hydrate of alumina, $\left.\begin{matrix}Al_2\\H_3\end{matrix}\right\}\Theta_3$; anhydrous alumina, $\left.\begin{matrix}Al_2\\Al_2\end{matrix}\right\}\Theta_3$; antimonic hydrate, $\left.\begin{matrix}Sb\\H_3\end{matrix}\right\}\Theta_3$; antimonic oxide, $\left.\begin{matrix}Sb\\Sb\end{matrix}\right\}\Theta_3$; teroxide of bismuth, $\left.\begin{matrix}Bi\\Bi\end{matrix}\right\}\Theta_3$.

Certain triatomic bases may be represented as monatomic, by supposing a portion of the oxygen to be associated with the positive radical; thus, sesquioxide of uranium, $U_4\Theta_3$, may be represented as protoxide of uranyl, $\left.\begin{matrix}U_2\Theta\\U_2\Theta\end{matrix}\right\}\Theta$; and teroxide of antimony, $Sb_2\Theta_3$, as protoxide of antimonyl, $\left.\begin{matrix}Sb\Theta\\Sb\Theta\end{matrix}\right\}\Theta$. Nonbasic bioxides, or peroxides, may be represented in a similar manner; *e. g.*, peroxide of hydrogen, $= \left.\begin{matrix}H\Theta\\H\end{matrix}\right\}\Theta$.

B. Alcohols.—These bodies, all of which belong to organic chemistry, are also monatomic, biatomic, or triatomic. The *primary monatomic alcohols*, or *alcohols proper*, are derived from water by the replacement of 1 atom of hydrogen by a hydrocarbon of the form $\bar{C}_nH_{2n+1}$; $\bar{C}_nH_{2n-1}$; or $\bar{C}_nH_{2n-7}$.

a. Alcohols containing radicals of the form $\bar{C}_nH_{2n+1}$. The number of these at present known is ten, viz.:—

Methylic alcohol, wood-spirit, or hydrate of methyl (protyl). $\bar{C}H_4\Theta = \left.\begin{matrix}\bar{C}H_3\\H\end{matrix}\right\}\Theta$.

Ethylic alcohol, spirit of wine, or hydrate of ethyl (deutyl). $\bar{C}_2H_6\Theta = \left.\begin{matrix}\bar{C}_2H_5\\H\end{matrix}\right\}\Theta$.

Propylic alcohol, or hydrate of trityl.......................... $\bar{C}_3H_8\Theta = \left.\begin{matrix}\bar{C}_3H_7\\H\end{matrix}\right\}\Theta$.

Butylic alcohol, or hydrate of tetryl.......................... $\bar{C}_4H_{10}\Theta = \left.\begin{matrix}\bar{C}_4H_9\\H\end{matrix}\right\}\Theta$.

Amylic alcohol, or hydrate of amyl (pentyl).................. $\bar{C}_5H_{12}\Theta = \left.\begin{matrix}\bar{C}_5H_{11}\\H\end{matrix}\right\}\Theta$.

Caproic alcohol, or hydrate of hexyl.......................... $\bar{C}_6H_{14}\Theta = \left.\begin{matrix}\bar{C}_6H_{10}\\H\end{matrix}\right\}\Theta$.

Caprylic alcohol, or hydrate of octyl.......................... $\bar{C}_8H_{18}\Theta = \left.\begin{matrix}\bar{C}_8H_{17}\\H\end{matrix}\right\}\Theta$.

Cetylic alcohol, or hydrate of cetyl.......................... $\bar{C}_{16}H_{34}\Theta = \left.\begin{matrix}\bar{C}_{16}H_{33}\\H\end{matrix}\right\}\Theta$.

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* The radical stibethyl is biatomic, like arsenethyl (p. 695).

Cerylic alcohol, or hydrate of ceryl.............................. $C_{27}H_{56}\Theta = \left.\begin{matrix}C_{27}H_{55}\\ H\end{matrix}\right\}\Theta.$

Melissic alcohol, or hydrate of melissyl.............................. $C_{30}H_{62}\Theta = \left.\begin{matrix}C_{30}H_{61}\\ H\end{matrix}\right\}\Theta.$

The first of these liquids is found among the products of the destructive distillation of wood; the second, third, fourth, and fifth, are formed by the fermentation of saccharine substances; caprylic alcohol is obtained by saponifying castor-oil with hydrate of potash and distilling the product with excess of the alkali at a high temperature; cetylic alcohol is obtained from spermaceti: cerylic alcohol from Chinese wax, and melissic alcohol from bees-wax.

Compounds, whose formulæ differ from one another by $n\,.\,CH_2$, are said to be *homologous: e. g.*, the alcohols, the fatty acids (p. 701), the compound ethers (p. 706), &c.

β. Alcohols containing radicals of the form C_nH_{2n-1}: —

Acrylic or allylic alcohol, $C_3H_6\Theta = \left.\begin{matrix}C_3H_5\\ H\end{matrix}\right\}\Theta.$ This is the only term of the series at present known.

γ. Alcohols containing the radicals, C_nH_{2n-7}: — Of this series, there are two isomeric groups, distinguished by their behaviour with oxidizing agents, the bodies of the one group being thereby converted into aldehydes, the others not. To the first group belong: —

Benzoic alcohol.. $C_7H_8\Theta = \left.\begin{matrix}C_7H_7\\ H\end{matrix}\right\}\Theta.$

Cuminic alcohol .... $C_{10}H_{14}\Theta = \left.\begin{matrix}C_{10}H_{13}\\ H\end{matrix}\right\}\Theta.$

To the second: —

Phenylic alcohol, carbazotic acid, or hydrate of phenyl .... $C_6H_6\Theta = \left.\begin{matrix}C_6H_5\\ H\end{matrix}\right\}\Theta.$

Cresylic alcohol.. $C_7H_8\Theta = \left.\begin{matrix}C_7H_7\\ H\end{matrix}\right\}\Theta.$

All these alcohols contain 1 atom of hydrogen replaceable by a metal; thus: common alcohol, treated with potassium, gives off one sixth of its hydrogen, and yields ethylate of potassium, $\left.\begin{matrix}C_2H_5\\ K\end{matrix}\right\}\Theta.$ It is not found possible to replace another atom of hydrogen in a similar manner.

Biatomic Alcohols, or *Glycols.* — The general formula of these compounds is $\left.\begin{matrix}C_nH_{2n}\\ H_2\end{matrix}\right\}\Theta_2.$ Three of them have been obtained, viz., ethylic glycol, $\left.\begin{matrix}C_2H_4\\ H_2\end{matrix}\right\}\Theta_2$; propylic glycol, $\left.\begin{matrix}C_3H_6\\ H_2\end{matrix}\right\}\Theta_2$; and amylic glycol, $\left.\begin{matrix}C_5H_{10}\\ H_2\end{matrix}\right\}\Theta_2.$ The 2 at. hydrogen in each of these formulæ may be replaced by other radicals, positive or negative; so that the glycols are bibasic and biacid. By mixing iodide of ethylene, $C_2H_4.I_2$ with 2 atoms of acetate of silver, and distilling the product, a distillate of acetate of glycol is obtained, while iodide of silver remains behind: —

$$C_2H_4I_2 + 2\underbrace{\left(\left.\begin{matrix}C_2H_3\Theta\\ Ag\end{matrix}\right\}\Theta\right)}_{\text{Acetate of silver.}} = 2\,AgI + \underbrace{\left.\begin{matrix}C_2H_4\\ (C_2H_3\Theta)_2\end{matrix}\right\}\Theta_2}_{\text{Acetate of glycol.}};$$

and acetate of glycol distilled with hydrate of potash yields glycol and acetate of potash: —

$$\left.\begin{matrix}C_2H_4\\ (C_2H_3\Theta)_2\end{matrix}\right\}\Theta_2 + 2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}\Theta\right) = \left.\begin{matrix}C_2H_4\\ H_2\end{matrix}\right\}\Theta_2 + 2\left(\left.\begin{matrix}C_2H_3\Theta\\ K\end{matrix}\right\}\Theta\right).$$

The propylic and amylic glycols are obtained in a similar manner with bromide of propylene and bromide of amylene.

Triatomic Alcohols, or *Glycerines.*—The general formula of these compounds is $\left.\begin{matrix}\text{Ȼ}_nH_{2n-1}\\H_3\end{matrix}\right\}\text{Ɵ}_3$. The three atoms of hydrogen which they contain may be wholly or partly replaced by radicals positive or negative. One term of the series has been long known, viz.: ordinary glycerine, $\text{Ȼ}_3H_8\text{Ɵ}_3 = \text{Ȼ}_3\left.\begin{matrix}H_5\\H_3\end{matrix}\right\}\text{Ɵ}_3$. The neutral fats, olein, stearin, palmitin, &c., consist of glycerin, in which the 3 atoms of free hydrogen are replaced by acid radicals; *e. g.*, stearin, $\text{Ȼ}_{57}H_{110}\text{Ɵ}_6 = \left.\begin{matrix}\text{Ȼ}_3H_5\\(\text{Ȼ}_{18}H_{35}\text{Ɵ})_3\end{matrix}\right\}\text{Ɵ}_3$. A great number of similar compounds have been formed artificially by heating glycerine with acids. Conversely, when neutral fats, stearin for example, are heated with hydrate of potash, or other metallic oxides, the acid radical passes to the metal, forming a salt, and glycerine is formed, *e. g.*,

$$\left.\begin{matrix}\text{Ȼ}_3H_5\\(\text{Ȼ}_{18}H_{35}\text{Ɵ})_3\end{matrix}\right\}\text{Ɵ}_3 + 3\left(\begin{matrix}K\\H\end{matrix}\text{Ɵ}\right) = 3\left(\begin{matrix}\text{Ȼ}_{18}H_{35}\text{Ɵ}\\K\end{matrix}\right)\text{Ɵ}_3 + \left.\begin{matrix}\text{Ȼ}_3H_5\\H_3\end{matrix}\right\}\text{Ɵ}_3.$$

This is the process of saponification. Glycerine may also be formed synthetically, viz. by heating the terbromide of allyl, $\text{Ȼ}_3H_5Br_3$, with acetate of silver. Teracetate of glycerine (triacetin) is thus formed; and this, when heated with hydrate of baryta, yields glycerine. The other glycerines have not yet been obtained in the free state; but the acetate of ethyl-glycerine, $\left.\begin{matrix}\text{Ȼ}_2H_3\\(\text{Ȼ}_2H_3\text{Ɵ})_3\end{matrix}\right\}\text{Ɵ}_3$, is obtained at the same time as glycol, by the action of iodide of ethylene on acetate of silver.

The *secondary alcohols,* or *Ethers,* bear the same relation to the primary alcohols that anhydrous metallic oxides bear to the hydrates; *e. g.*, amylic alcohol, $\left.\begin{matrix}\text{Ȼ}_5H_{11}\\H\end{matrix}\right\}\text{Ɵ}$; amylic ether, $\left.\begin{matrix}\text{Ȼ}_5H_{11}\\\text{Ȼ}_5H_{11}\end{matrix}\right\}\text{Ɵ}$.

There are likewise ethers containing two different radicals; *e.g.*, methyl-amylic ether, $\left.\begin{matrix}\text{Ȼ}H_3\\\text{Ȼ}_5H_{11}\end{matrix}\right\}\text{Ɵ}$. Ethers may be formed by the action of the iodides of methyl, ethyl, &c., on alcohols in which 1 atom of hydrogen is replaced by potassium; thus, common alcohol treated with potassium gives off hydrogen, and yields $\text{Ȼ}_2H_5K\text{Ɵ}$; and this compound, treated with iodide of amyl, yields ethyl-amylic ether:—

$$\left.\begin{matrix}\text{Ȼ}_2H_5\\K\end{matrix}\right\}\text{Ɵ} + \text{Ȼ}_5H_{11}I = KI + \left.\begin{matrix}\text{Ȼ}_2H_5\\\text{Ȼ}_5H_{11}\end{matrix}\right\}\text{Ɵ}.$$

The same potassium-alcohol, treated with iodide of ethyl, yields common ether:—

$$\left.\begin{matrix}\text{Ȼ}_2H_5\\K\end{matrix}\right\}\text{Ɵ} + \text{Ȼ}_2H_5.I = KI + \left.\begin{matrix}\text{Ȼ}_2H_5\\\text{Ȼ}_2H_5\end{matrix}\right\}\text{Ɵ}.$$

Ethers are also formed by the action of strong sulphuric acid on the alcohols, as will be more fully explained hereafter.

C. — *Aldehydes.* — These compounds differ from the alcohols, in containing 2 atoms of hydrogen less. Thus, to an alcohol, $\left.\begin{matrix}\text{Ȼ}_nH_{2n+1}\\H\end{matrix}\right\}\text{Ɵ}$, there corresponds an aldehyde, $\left.\begin{matrix}\text{Ȼ}_nH_{2n-1}\\H\end{matrix}\right\}\text{Ɵ}$. They are obtained by the action of oxidizing agents on the alcohols. Thus, common alcohol, treated with bichromate of potash and sulphuric acid, yields ethylic or acetic aldehyde, $\left.\begin{matrix}\text{Ȼ}_2H_3\\H\end{matrix}\right\}\text{Ɵ}$.

There are likewise aldehydes corresponding to the other series of alcohols. Thus, to the alcohols containing the radicals, Ȼ_nH_{2n-7}, there correspond aldehydes containing radicals of the form $\bar{C}_nH_{2n-9}$. Oil of bitter almonds, $\bar{C}_7H_6\Theta = \left.\begin{matrix}\bar{C}_7H_5\\ H\end{matrix}\right\}\Theta$, belongs to the series.

The aldehydes are especially distinguished by forming crystalline compounds with the alkaline bisulphites; *e.g.*, sulphite of acetosyl and sodium, $\bar{C}_2H_3Na\Theta, \bar{S}\Theta_2 = \left.\begin{matrix}\bar{S}\Theta\\ \bar{C}_2H_3 . Na\end{matrix}\right\}\Theta_2$.

One atom of hydrogen in the radical of an aldehyde may be replaced by an alcohol radical; the compounds thus produced are called *ketones*. Thus, acetone, $\bar{C}_3H_6\Theta$, the ketone of the acetic series, is $\left.\begin{matrix}\bar{C}_2H_2(\bar{C}H_3)\\ H\end{matrix}\right\}\Theta$.

ACIDS, OR NEGATIVE OXIDES. — These, like the positive oxides, are divided into primary or hydrated, and secondary or anhydrous. Thus, hydrated nitric acid, $\left.\begin{matrix}N\Theta_2\\ H\end{matrix}\right\}\Theta$; anhydrous nitric acid, $\left.\begin{matrix}N\Theta_2\\ N\Theta_2\end{matrix}\right\}\Theta$.

Acids are also monatomic, like nitric acid just noticed, and acetic acid, $\left.\begin{matrix}\bar{C}_2H_3\Theta\\ H\end{matrix}\right\}\Theta$; biatomic, like sulphuric acid, $\left.\begin{matrix}\bar{S}\Theta_2\\ H_2\end{matrix}\right\}\Theta_2$; or triatomic, as phosphoric acid, $\left.\begin{matrix}P\Theta\\ H_3\end{matrix}\right\}\Theta_3$; citric acid, $\left.\begin{matrix}\bar{C}_6H_5\Theta_4\\ H_3\end{matrix}\right\}\Theta_3$.

A monatomic hydrated acid, having only one atom of replaceable hydrogen, is necessarily monobasic; a biatomic acid, having two atoms of replaceable hydrogen, is generally (but not necessarily) bibasic; a triatomic acid, generally tribasic. The determination of the basicity of an acid is a matter of some difficulty. In many cases, the formation or non-formation of acid and double salts may serve as a distinction. Thus, tartaric acid, which is a bibasic acid, $\left.\begin{matrix}\bar{C}_4H_4\Theta_4\\ H_2\end{matrix}\right\}\Theta_2$, forms a neutral tartrate of potash, $\left.\begin{matrix}\bar{C}_4H_4\Theta_4\\ K_2\end{matrix}\right\}O_2$, and an acid tartrate, $\left.\begin{matrix}\bar{C}_4H_4\Theta_4\\ KH\end{matrix}\right\}\Theta_2$; so, likewise, sulphuric acid forms $\bar{S}K_2\Theta_4$, and $\bar{S}KH\Theta_4$; whereas nitric acid, having but one atom of hydrogen, forms but one potash-salt, viz., $NK\Theta_3$. But acetic acid, generally regarded as monobasic, $\bar{C}_2H_4\Theta_2 = \left.\begin{matrix}\bar{C}_2H_3\Theta\\ H\end{matrix}\right\}\Theta$, also forms, not only a neutral potash salt, $\bar{C}_2H_3K\Theta_2$, but likewise, an acid potash-salt, usually represented by the formula, $\bar{C}_2H_3K\Theta_2 . \bar{C}_2H_4\Theta_2$; but if the formula of acetic acid be doubled, making it $\bar{C}_4H_8\Theta_4$, the neutral potash-salt will be $\bar{C}_4H_6K_2\Theta_4$, and the acid salt, $\bar{C}_4H_6(KH)\Theta_4$. Acetic acid will thus be represented as a bibasic acid; and in fact, this quantity, $\bar{C}_4H_8\Theta_4$ (= 120), is the equivalent of $\bar{S}H_2\Theta_4$ (= 98), that is to say, it saturates the same quantity of potash. Why, then, is acetic acid universally regarded as monobasic? On this point, we shall quote the observations of Gerhardt: —

"The basicity of acids is a question, not of equivalents, but of molecules. . . . If we examine, *under the same volume*, the composition of the vapour of certain volatile bodies, corresponding to the acids, and compare together the similar terms, such as the chlorides of the acid radicals, or the neutral compound ethers, we observe perfectly regular differences, which are always related to the chemical properties of the corresponding bodies: thus, —

$$2\text{ vol. of}\begin{cases}\text{Chloride of acetyl............ contain } Cl . \bar{C}_2H_3\Theta.\\ \text{Chloride of sulphuryl........ '' } Cl_2 . \bar{S}\Theta_2.\end{cases}$$

$$2\text{ vol. of}\begin{cases}\text{Acetate of methyl............ contain } \left.\begin{matrix}\bar{C}_2H_3\Theta\\ \bar{C}H_3\end{matrix}\right\}\Theta.\\ \text{Sulphate of methyl.......... '' } \left.\begin{matrix}\bar{S}\Theta_2\\ (\bar{C}H_3)_2\end{matrix}\right\}\Theta_2.\end{cases}$$

In the same volume, therefore, chloride of acetyl contains the radical chlorine once, while chloride of sulphuryl contains it twice: In the same volume, again, sulphate of methyl contains twice the quantity of methyl that is contained in the acetate. With these differences of composition of the chlorides and neutral ethers, are connected other properties, such as the following:—Acetic acid forms but one compound ether (p. 705), whereas sulphuric acid forms two, a neutral and an acid ether; acetic acid forms but one amide (p. 714); sulphuric acid forms several, &c. In short, on inquiring what are the smallest quantities of the radicals, acetyl and sulphuryl, that are concerned in chemical metamorphoses, we find that they are $\text{Ȼ}_2H_3\Theta$, equivalent to H, and $S\Theta_2$ equivalent to H_2; hence, we are led to represent the molecule of acetic acid as monatomic, and that of sulphuric acid as biatomic."

The principal monobasic inorganic acids are nitric, $\left.\begin{matrix}N\Theta_2\\H\end{matrix}\right\}\Theta$, hypochlorous, $\left.\begin{matrix}Cl\\H\end{matrix}\right\}\Theta$, chloric, $\left.\begin{matrix}Cl\Theta_2\\H\end{matrix}\right\}\Theta$, and metaphosphoric, $\left.\begin{matrix}P\Theta_2\\H\end{matrix}\right\}\Theta$.

Of monobasic organic acids, the most important are the so-called fatty acids, whose general formula is—

$$\text{Ȼ}_nH_{2n}\Theta_2 = \left.\begin{matrix}\text{Ȼ}_nH_{2n-1}\Theta\\H\end{matrix}\right\}\Theta.$$

They correspond to the alcohols $\text{Ȼ}_nH_{2n+1}\Theta$, and those which contain the same number of carbon atoms as the known alcohols may be obtained from the latter by the action of oxidizing agents, such as chromic acid. The number of these acids at present known to exist is sixteen, viz.:—

Formic acid	$\text{Ȼ}_1H_2\Theta_2$	Œnanthylic acid	$\text{Ȼ}_7H_{14}\Theta_2$	Palmitic acid	$\text{Ȼ}_{16}H_{32}\Theta_2$
Acetic "	$\text{Ȼ}_2H_4\Theta_2$	Caprylic "	$\text{Ȼ}_8H_{16}\Theta_2$	Stearic "	$\text{Ȼ}_{18}H_{36}\Theta_2$
Propionic "	$\text{Ȼ}_3H_6\Theta_2$	Pelargonic "	$\text{Ȼ}_9H_{18}\Theta_2$	Cerotic "	$\text{Ȼ}_{27}H_{54}\Theta_2$
Butyric "	$\text{Ȼ}_4H_8\Theta_2$	Rutic or capric	$\text{Ȼ}_{10}H_{20}\Theta_2$	Melissic "	$\text{Ȼ}_{30}H_{60}\Theta_2$
Valerianic	$\text{Ȼ}_5H_{10}\Theta_2$	Lauric "	$\text{Ȼ}_{12}H_{24}\Theta_2$		
Caproic "	$\text{Ȼ}_6H_{12}\Theta_2$	Myristic "	$\text{Ȼ}_{14}H_{28}\Theta_2$		

These acids occur in the vegetable and animal organism; they are formed by the saponification of fats, and by the action of oxidizing agents on fatty and waxy matters, and on albumin, fibrin, casein, &c. The first ten acids of the series are liquid at ordinary temperatures; the next four are solid fats; the last two are waxy. Cerotic acid is obtained from Chinese wax; melissic acid from bees'-wax.

A second series of monobasic organic acids consists of acids whose radical is of the form $\text{Ȼ}_nH_{2n-3}\Theta$; *e.g.*, oleic acid, $\text{Ȼ}_{18}H_{34}\Theta_2 = \left.\begin{matrix}\text{Ȼ}_{18}H_{33}\\H\end{matrix}\right\}\Theta$, obtained by the saponification of various fixed oils. A third series consists of acids whose radical has the form $\text{Ȼ}_nH_{2n-9}\Theta$. These are called the *aromatic acids;* only three of them are known, viz. benzoic acid, $\left.\begin{matrix}\text{Ȼ}_7H_5\Theta\\H\end{matrix}\right\}\Theta$; toluic acid, $\left.\begin{matrix}\text{Ȼ}_8H_7\Theta\\H\end{matrix}\right\}\Theta$, and cuminic acid, $\left.\begin{matrix}\text{Ȼ}_{10}H_{11}\Theta\\H\end{matrix}\right\}\Theta$.

There are a few monatomic organic acids not included in either of these groups, among which must be particularly mentioned cyanic acid, $\left.\begin{matrix}\text{Ȼ}N\\H\end{matrix}\right\}\Theta$. The cyanates are formed from the cyanides by oxidation; thus, cyanide of potassium fused with oxide of lead, or bioxide of manganese, yields cyanate of potash, $\text{Ȼ}NK\Theta$.

Bibasic acids.—These acids, as already observed, generally form two salts, a neutral and an acid salt, and are peculiarly inclined to form double salts; *e.g.* potassio-cupric sulphate, $\left.\begin{matrix}S\Theta_2\\KCu\end{matrix}\right\}\Theta_2$; tartrate of potash and soda, $\left.\begin{matrix}\text{Ȼ}_4H_4\Theta_4\\KNa\end{matrix}\right\}\Theta_2$.

With the alcohols they form two compound ethers, a neutral and an acid ether;

e. g., neutral oxalate of ethyl, $\left.\begin{matrix}Ȼ_2Θ_2\\(Ȼ_2H_5)_2\end{matrix}\right\}Θ_2$; acid oxalate of ethyl, or oxalovinic acid, $\left.\begin{matrix}Ȼ_2Θ_2\\H(Ȼ_2H_2)\end{matrix}\right\}Θ_2$.

Within the same vapour volume, the neutral ethers of the bibasic acids contain twice as much of the alcohol-radical as the neutral ethers of the monobasic acids (p. 706). Thus, 2 vols. oxalate of ethyl = $\left.\begin{matrix}Ȼ_2Θ_2\\(Ȼ_2H_5)_2\end{matrix}\right\}Θ$; 2 vols. benzoate of ethyl = $\left.\begin{matrix}Ȼ_7H_5Θ\\Ȼ_2H_5\end{matrix}\right\}Θ$.

The chlorides of bibasic acids (obtained by the action of pentachloride of phosphorus on the acids) *contain, within a given vapour volume, twice as much chlorine as the chlorides of monobasic acids* (p. 708).

The principal bibasic inorganic acids are carbonic, $\left.\begin{matrix}ȻΘ\\H_2\end{matrix}\right\}Θ_2$; sulphurous, $\left.\begin{matrix}SΘ\\H_2\end{matrix}\right\}Θ_2$; sulphuric, $\left.\begin{matrix}SΘ_2\\H_2\end{matrix}\right\}Θ_2$; and chromic acid, $\left.\begin{matrix}Cr_2Θ^2\\H_2\end{matrix}\right\}Θ_2$. Pyro-phosphoric acid, $P_2H_4Θ_7$, may be regarded as bibasic acid, containing the radical, $P_2H_2Θ_5$; viz., $\left.\begin{matrix}P_2H_2Θ_5\\H_2\end{matrix}\right\}Θ_2$; or as a compound of metaphosphoric and ordinary phosphoric acid.

The greater number of the bibasic organic acids may be arranged in three groups, viz.:—

α.—Acids whose general formula is $\left.\begin{matrix}Ȼ_nH_{2n-4}Θ_2\\H_2\end{matrix}\right\}Θ_2$. Eight of these are known, viz.:—Oxalic acid, $\left.\begin{matrix}Ȼ_2Θ_2\\H_2\end{matrix}\right\}Θ_2$; succinic acid, $(Ȼ_4)$; pyro-tartaric, $(Ȼ_5)$; adipic, $(Ȼ_6)$; pimelic, $(Ȼ_7)$; suberic, $(Ȼ_8)$; anchoic, $(Ȼ_9)$; and sebacic acid, $(Ȼ_{10})$. They are formed by the action of oxidizing agents on fatty matters, and are related to the monobasic fatty acids, $Ȼ_nH_{2n}Θ_4$, by the relation —

$$Ȼ_nH_{2n-2}Θ_4 = ȻΘ_2 + Ȼ_{n-1}H_{2n-2}Θ_2$$

e. g.,

$$\underbrace{Ȼ_4H_6Θ_4}_{\text{Succinic acid.}} = ȻΘ_2 + \underbrace{Ȼ_3H_6Θ_4}_{\text{Propionic acid.}}$$

β.—General formula: $\left.\begin{matrix}(Ȼ_nH_{2n-1}Θ_2)_2\\H_2\end{matrix}\right\}Θ_2$. For example, lactic acid = $Ȼ_6H_{12}Θ_6$ = $\left.\begin{matrix}(Ȼ_3H_5Θ_2)_2\\H_2\end{matrix}\right\}Θ_2$.

γ.—General formula: $\left.\begin{matrix}Ȼ_nH_{2n-10}Θ_2\\H_2\end{matrix}\right\}Θ_2$. Two acids of this group are known, viz., phthalic acid, $Ȼ_8H_6Θ_4$, obtained by the action of nitric acid on bichloride of napthalin, and insolinic acid, $Ȼ_9H_8Θ_4$, by the action of chromic acid on cuminic acid. They are related to the aromatic acids in the same manner as the acids α to the fatty acids. Thus:—

$$\underbrace{Ȼ_8H_8Θ_4}_{\text{Insolinic acid.}} = ȻΘ_2 + \underbrace{Ȼ_8H_8Θ_2}_{\text{Toluic acid.}}.$$

Of bibasic acids not included in the preceding groups, the most important are malic acid, $Ȼ_4H_6Θ_5 = \left.\begin{matrix}Ȼ_4H_4Θ_3\\H_2\end{matrix}\right\}Θ_2$; and tartaric acid, $Ȼ_4H_6Θ_6 = \left.\begin{matrix}Ȼ_4H_4Θ_4\\H_2\end{matrix}\right\}Θ_2$.

Tribasic acids. — These acids, containing three atoms of replaceable hydrogen, form three kinds of salts, viz., one neutral, and two acid salts. Thus, from tribasic phosphoric acid, $PH_3Θ_4 = \left.\begin{matrix}PΘ\\H_3\end{matrix}\right\}Θ_3$ are formed $PH_2KΘ_4$, $PHK_2Θ_4$, and $PK_3Θ_4$.

With alcohols they form three compound ethers. Phosphoric acid and common alcohol yield ethylophosphoric acid, $PH_2(Ꞓ_2H_5)\Theta_4$; bi-ethylophosphoric acid, $PH(Ꞓ_2H_5)_2\Theta_4$; phosphoric ether, $P(Ꞓ_2H_5)_3\Theta_4$.

The neutral ethers of tribasic acids contain, within a given vapour volume, three times as much of the alcohol radical as the ethers of the monobasic acids Thus, 2 vols. citric ether contain $\left.\begin{matrix}Ꞓ_6H_5\Theta_4\\(Ꞓ_2H_5)_3\end{matrix}\right\}\Theta_3$; and 2 vols. acetic ether contain $\left.\begin{matrix}Ꞓ_2H_3\Theta\\Ꞓ_2H_5\end{matrix}\right\}\Theta$.

The chlorides of the tribasic acid radicals contain, within a given volume, three times as much chlorine as the chlorides of the monobasic acid radicals. Thus, 2 vols. chloride of phosphoryl (oxychloride of phosphorus) contain $P\Theta . Cl_3$; and 2 vols. chloride of benzoyl contain $Ꞓ_7H_5\Theta . Cl$.

The tribasic mineral acids are,—boracic acid, $BH_3\Theta_3$; phosphorous acid, $PH_3\Theta_3$; phosphoric acid, $PH_3\Theta_4$; and arsenic acid, $AsH_3\Theta_4$.

Five tribasic organic acids are known, viz.:—

Cyanuric acid	$Ꞓ_6H_3N_3\Theta_3 = \left.\begin{matrix}Cy_3\\H_3\end{matrix}\right\}\Theta_3.$
Citric acid	$Ꞓ_6H_8\Theta_7 = \left.\begin{matrix}Ꞓ_6H_5\Theta_4\\H_3\end{matrix}\right\}\Theta_3.$
Aconitic acid	$Ꞓ_6H_6\Theta_6 = \left.\begin{matrix}Ꞓ_6H_3\Theta_3\\H_3\end{matrix}\right\}\Theta_3.$
Meconic acid	$Ꞓ_7H_4\Theta_7 = \left.\begin{matrix}Ꞓ_7H\Theta_4\\H_3\end{matrix}\right\}\Theta_3.$
Chelidonic acid	$Ꞓ_7H_4\Theta_6 = \left.\begin{matrix}Ꞓ_7H\Theta_3\\H_3\end{matrix}\right\}\Theta_3.$

Cyanuric acid may be regarded as a triple molecule of cyanic acid. It is formed by the destructive distillation of uric acid, by the action of chlorine gas on urea, and by the action of water on fixed chloride of cyanogen, Cy_3Cl_3. Aconitic acid is obtained by the destructive distillation of citric acid. Meconic acid is contained in opium, and chelidonic acid in the *chelidonium majus.*

Conjugated acids.—This name is given to acids containing a conjugated radical. Thus, there are *chloro-*, *bromo-*, and *iodo-conjugated* acids, containing chlorine, bromine, or iodine in place of hydrogen in the radical; *e. g.*, chloracetic acid, $\left.\begin{matrix}Ꞓ_2(Cl_2H)\Theta\\H\end{matrix}\right\}\Theta$; terchloracetic acid, $\left.\begin{matrix}Ꞓ_2Cl_3\Theta\\H\end{matrix}\right\}\Theta$: *nitro-conjugated* acids, containing $N\Theta_2$; *e. g.*, nitro-benzoic acid, $\left.\begin{matrix}Ꞓ_7H_4(N\Theta_2)\Theta\\H\end{matrix}\right\}\Theta$: *sulpho-conjugated* acids, containing $Ꞩ\Theta_2$; *e. g.*, sulpho-benzoic acid, $\left.\begin{matrix}Ꞓ_7H_4(Ꞩ\Theta_2)\Theta\\H_2\end{matrix}\right\}\Theta_2$, &c.

These acids are formed by the action of sulphuric acid, nitric acid, chlorine, &c., on the primitive acids:—

$$\left.\begin{matrix}Ꞓ_7H_5\Theta\\H\end{matrix}\right\}\Theta + \left.\begin{matrix}N\Theta_2\\H\end{matrix}\right\}\Theta = \left.\begin{matrix}H\\H\end{matrix}\right\}\Theta + \left.\begin{matrix}Ꞓ_7H_4(N\Theta_2)\Theta\\H\end{matrix}\right\}\Theta.$$

$$\left.\begin{matrix}Ꞓ_7H_5\Theta\\H\end{matrix}\right\}\Theta + \left.\begin{matrix}Ꞩ\Theta_2\\H_2\end{matrix}\right\}\Theta_2 = \left.\begin{matrix}H\\H\end{matrix}\right\}\Theta + \left.\begin{matrix}Ꞓ_7H_4(Ꞩ\Theta_2)\Theta\\H_2\end{matrix}\right\}\Theta_2.$$

α.—*Amidogen acids.*—These are derived from hydrate of ammonium, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}\Theta$, by the substitution of an acid radical for two or more atoms of the hydrogen in ammonium. Thus:—

Sulphamic acid .... $SH_3N\Theta_3 = \left.\begin{matrix}NH_2S\Theta_2\\ H\end{matrix}\right\}\Theta.$

Phosphamic acid .... $PH_2N\Theta_2 = \left.\begin{matrix}NH(P\Theta)\\ H\end{matrix}\right\}\Theta.$

Osmiamic acid .... $Os_2HN\Theta_3 = \left.\begin{matrix}N(Os_2\Theta_2)\\ H\end{matrix}\right\}\Theta.$

Oxamic acid................................. $C_2H_3N\Theta_3 = \left.\begin{matrix}NH_2(C_2\Theta_2)\\ H\end{matrix}\right\}\Theta.$

These acids are formed by the action of ammonia on the anhydrides, or by the action of heat on the acid ammonia-salts of bibasic acids, an atom of water being thus eliminated: —

$$\underbrace{\left.\begin{matrix}C_2\Theta_2\\ H..(NH_4)\end{matrix}\right\}\Theta_2}_{\text{Acid oxalate of ammonia.}} - H_2\Theta = \underbrace{\left.\begin{matrix}NH_2(C_2\Theta_2)\\ H\end{matrix}\right\}\Theta.}_{\text{Oxamic acid.}}$$

ANHYDROUS ACIDS, OR ANHYDRIDES. — These compounds are formed by the substitution of an acid radical for the whole of the hydrogen in one or two molecules of water, thus: — citric anhydride, $N_2\Theta_5 = \left.\begin{matrix}N\Theta_2\\ N\Theta_2\end{matrix}\right\}\Theta$; sulphuric anhydride, $S\Theta_3 = S\Theta_2 . \Theta$; phosphoric anhydride, $P_2\Theta_5 = \left.\begin{matrix}P\Theta\\ P\Theta\end{matrix}\right\}\Theta_3$.

Anhydrous nitric acid is obtained by the action of chlorine on dry nitrate of silver. The anhydrides of bibasic acids may be formed by the abstraction of water from the hydrated acids, either by heat or by the action of anhydrous phosphoric acid; *e. g.*: —

$$\underbrace{\left.\begin{matrix}C_4H_4\Theta_2\\ H_2\end{matrix}\right\}\Theta_2}_{\text{Succinic acid.}} - H_2\Theta = \underbrace{C_4H_4\Theta_2 . \Theta.}_{\text{Succinic anhydride.}}$$

The bibasic acids may, indeed, be supposed to contain water. Thus, succinic acid $= C_4H_4\Theta_2 . \Theta + H_2\Theta$. But the anhydrides of the monobasic acids cannot be obtained in this way; in fact, according to the formulæ of the unitary system, they do not contain water, and even supposing $H_2\Theta$ to be abstracted from them, the remainder will not be the formula of the anhydrides: thus, the formula of acetic acid being $\left.\begin{matrix}C_2H_3\Theta\\ H\end{matrix}\right\}\Theta$, the abstraction of $H_2\Theta$ would leave $C_2H_2\Theta$; whereas, the formula of anhydrous acetic acid is $\left.\begin{matrix}C_2H_3\Theta\\ C_2H_3\Theta\end{matrix}\right\}\Theta = 2 \times C_2H_3\Theta_{\frac{3}{2}}$. This is a fact which the ordinary formulæ do not explain. If the formula of hydrated acetic acid be $C_4H_4O_4 = C_4H_3O_3 . HO$, it is by no means evident why the HO should not be separated from it, and leave the anhydrous acid.

The anhydrides of organic monobasic acids are obtained by the action of the chlorides of their radicals on the alkaline salts of the acids; thus: —

$$\underbrace{\left.\begin{matrix}C_2H_3\Theta\\ K\end{matrix}\right\}\Theta}_{\text{Acetate of potash.}} + \underbrace{C_2H_3\Theta\ .\ Cl}_{\text{Chloride of acetyl.}} = KCl + \underbrace{\left.\begin{matrix}C_2H_3\Theta\\ C_2H_3\Theta\end{matrix}\right\}\Theta.}_{\text{Acetic anhydride.}}$$

There are some organic anhydrides containing two different radicals; thus, by the action of chloride of benzoyl on acetate of potash, aceto-benzoic anhydride is formed: —

$$\left.\begin{matrix}C_2H_3\Theta\\ K\end{matrix}\right\}\Theta + C_7H_5\Theta . Cl = KCl + \left.\begin{matrix}C_2H_3\Theta\\ C_7H_5\Theta\end{matrix}\right\}\Theta.$$

These compounds are resolved by heat into the simple anhydrides, thus:—

$$\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O+\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O=\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}+\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}O.$$

OXYGEN-SALTS, OR INTERMEDIATE OXIDES.—Salts are formed by the substitution of a metal or other positive radical for the basic hydrogen of an acid, and may therefore be regarded as water, the hydrogen of which is replaced partly by a basic, partly by an acid radical. If all the basic hydrogen of the acid is thus replaced, the salt is *neutral* or *normal;* if only part of the hydrogen is thus replaced, the salt is *acid;* and such salts may be regarded as compounds of neutral salts with the free acid, thus:—

$$\underbrace{2\Big(\left.\begin{matrix}SO_2\\NaH\end{matrix}\right\}O_2\Big)}_{\substack{\text{Bisulphate}\\\text{of soda.}}}=\underbrace{\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2}_{\substack{\text{Sulphuric}\\\text{acid.}}}+\underbrace{\left.\begin{matrix}SO_2\\Na_2\end{matrix}\right\}O_2.}_{\substack{\text{Neutral sul-}\\\text{phate of soda.}}}$$

$$\underbrace{\left.\begin{matrix}(C_2H_3O)_2\\KH\end{matrix}\right\}O_2}_{\substack{\text{Biacetate of}\\\text{potash.}}}=\underbrace{\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O}_{\substack{\text{Acetic}\\\text{acid.}}}+\underbrace{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O.}_{\substack{\text{Neutral acetate}\\\text{of potash.}}}$$

Basic salts may be regarded as compounds of a neutral salt and an oxide, or as double or triple molecules of water, in which the hydrogen is replaced by a positive radical in a larger proportion than is required to form a neutral salt; thus:—

$$\underbrace{\left.\begin{matrix}C_2H_3O\\Pb_3\end{matrix}\right\}O_2}_{\substack{\text{Subacetate}\\\text{of lead.}}}=\underbrace{\left.\begin{matrix}Pb\\Pb\end{matrix}\right\}O}_{\substack{\text{Oxide of}\\\text{lead.}}}+\underbrace{\left.\begin{matrix}C_2H_3O\\Pb\end{matrix}\right\}O.}_{\substack{\text{Neutral acetate}\\\text{of lead.}}}$$

$$\underbrace{\left.\begin{matrix}SO_2\\Cu_4\end{matrix}\right\}O_3}_{\substack{\text{Subsulphate}\\\text{of copper.}}}=\underbrace{\left.\begin{matrix}Cu\\Cu\end{matrix}\right\}O}_{\substack{\text{Oxide of}\\\text{copper.}}}+\underbrace{\left.\begin{matrix}Cu_2\\SO_2\end{matrix}\right\}O_2.}_{\substack{\text{Neutral sulphate}\\\text{of copper.}}}$$

In the neutral salts of sesquioxides, as in the oxides themselves, 3 at. hydrogen of the type water are replaced by 2 at. of the metal; thus—

$$\underbrace{\left.\begin{matrix}(NO_2)_3\\Fe_2\end{matrix}\right\}O_3;}_{\text{Ferric nitrate.}}\qquad\underbrace{\left.\begin{matrix}(SO_2)_3\\Fe_4\end{matrix}\right\}O_6.}_{\text{Ferric sulphate.}}$$

Compound ethers.—When the basic hydrogen of an acid is replaced by an alcohol-radical, the product is a compound ether; these compounds may also be regarded as alcohols in which one atom of hydrogen is replaced by an acid radical. As already observed, monobasic acids form but one compound ether; bibasic acids form two, a neutral and an acid ether; and tribasic acids, one neutral and two acid ethers. The acid ethers are true acids, and form salts. Thus, from sulphuric acid are formed—

Neutral sulphate of ethyl..................... = $\left.\begin{matrix}SO_2\\(C_2H_5)_2\end{matrix}\right\}O_2$, and

Acid sulphate of ethyl, or sulphovinic acid = $\left.\begin{matrix}SO_2\\H\\C_2H_5\end{matrix}\right\}O_2.$

The remaining atom of hydrogen in the latter may be replaced by K, Na, &c.

From citric acid are formed—

Neutral citrate of methyl........................ $\left.\begin{matrix}\text{Ꞓ}_6H_5\Theta_4\\(\text{Ꞓ}H_3)_3\end{matrix}\right\}\Theta_3.$

Citrobimethylic acid (monobasic)........................ $\left.\begin{matrix}\text{Ꞓ}_6H_5\Theta_4\\(\text{Ꞓ}H_3)_2\\H\end{matrix}\right\}\Theta_3.$

Citromonomethylic acid (bibasic) .... $\left.\begin{matrix}\text{Ꞓ}_6H_5\Theta_4\\\text{Ꞓ}H_3\\H_2\end{matrix}\right\}\Theta_3.$

The *glycerides* or *neutral fats* (p. 699) also belong to the compound ethers, being derived from a triatomic alcohol or glycerine by the substitution of an acid radical for the replaceable hydrogen; *e. g.*, triacetin $= \left.\begin{matrix}\text{Ꞓ}_3H_5\\(\text{Ꞓ}_2H_3\Theta)_3\end{matrix}\right\}\Theta_3$

SULPHIDES, SELENIDES, TELLURIDES.

The formulæ of these bodies are precisely similar to those of the oxides, being derived from hydrosulphuric acid, $\left.\begin{matrix}H\\H\end{matrix}\right\}\text{Ꞩ}$, &c., just as the oxides are derived from water. These series, however, especially the selenides and tellurides, are much less complete than that of the oxides.

The analogy between the metallic sulphides and oxides has been sufficiently pointed out in the preceding part of this work. The alkali-metals, potassium, sodium, &c., form hydrated sulphides, or hydro-sulphates, such as $\left.\begin{matrix}K\\H\end{matrix}\right\}\text{Ꞩ}$, $\left.\begin{matrix}Ba\\H\end{matrix}\right\}\text{Ꞩ}$, &c.; and anhydrous sulphides, $\left.\begin{matrix}K\\K\end{matrix}\right\}\text{Ꞩ}$, &c. Most of the other metals form only anhydrous sulphides.

The *alcoholic sulphides*, primary and secondary, bear the same relation to hydrosulphuric acid that the alcohols and ethers bear to water. The primary alcoholic sulphides, $\left.\begin{matrix}\text{Ꞓ}_nH_{2n+1}\\H\end{matrix}\right\}\text{Ꞩ}$, generally called *mercaptans*, are fetid oils, or crystalline solids, which are obtained by the action of the alkaline hydrosulphates on the chlorides of the alcohol radicals:—

$$\underbrace{\text{Ꞓ}_2H_5\,Cl}_{\text{Chloride of ethyl.}} + \left.\begin{matrix}K\\H\end{matrix}\right\}\text{Ꞩ} = KCl + \underbrace{\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{Ꞩ}}_{\text{Ethylic mercaptan.}};$$

or by the action of the same alkaline hydrosulphates on the sulphovinates or homologous salts:—

$$\left.\begin{matrix}\text{Ꞩ}\Theta_2\\K,\text{Ꞓ}_2H_5\end{matrix}\right\}\Theta_2 + \left.\begin{matrix}K\\H\end{matrix}\right\}\text{Ꞩ} = \left.\begin{matrix}\text{Ꞩ}\Theta_2\\K_2\end{matrix}\right\}\Theta_2 + \left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{Ꞩ}.$$

The basic hydrogen in the mercaptans may be replaced by metals, forming compounds called *mercaptides; e g.*, $\left.\begin{matrix}\text{Ꞓ}_2H_5\\Hg\end{matrix}\right\}\text{Ꞩ}$.

The secondary alcoholic sulphides or hydrosulphuric ethers are obtained by the action of the anhydrous alkaline sulphides on the chlorides of the alcohol-radicals:—

$$2\text{Ꞓ}_2H_5Cl + \left.\begin{matrix}K\\K\end{matrix}\right\}\text{Ꞩ} = 2KCl + \left.\begin{matrix}\text{Ꞓ}_2H_5\\\text{Ꞓ}_2H_5\end{matrix}\right\}\text{Ꞩ}.$$

Sulphur-acids.—The mineral sulphur-acids are but little known in the hydrated state. The anhydrous sulphur-acids are analogous to the oxygen-acids. Thus, sulpharsenious acid, $\left.\begin{matrix}As\\As\end{matrix}\right\}S_3$, sulpharsenic acid, $\left.\begin{matrix}As\\As\end{matrix}\right\}S_5$, the arsenic being triatomic in the former, and pentatomic in the latter.

But few organic sulphur-acids have been obtained. Hydrosulphocyanic acids, $CNHS = \left.\begin{matrix}Cy\\H\end{matrix}\right\}S$, is analogous to cyanic acid, $\left.\begin{matrix}Cy\\H\end{matrix}\right\}O$. Its potassium-salt is obtained by heating sulphur with ferrocyanide of potassium (p. 377).

Thiacetic acid $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S$, is obtained by the action of pentasulphide of phosphorus on acetic acid: —

$$5\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O\right) + P_2S_5 = P_2O_5 + 5\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S\right).$$

This reaction is instructive when viewed in relation to that of pentachloride of phosphorus on acetic acid; the latter giving rise to two chlorides, $C_2H_3O.Cl$, and HCl, whereas the action of the sulphide of phosphorus yields not two, but one sulphur compound, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S$. A similar difference is observed in the action of the sulphide and chloride of phosphorus on alcohol, the former producing a single compound, viz., mercaptan, the sulphide of ethyl and hydrogen, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$, the latter producing two separate compounds, viz., C_2H_5Cl, and HCl. This difference of action shows in a striking manner the propriety of representing the oxides and sulphides by a type containing two atoms of hydrogen, and the chlorides, bromides, &c., by a type containing only one atom of hydrogen.

Sulphur-salts.—These compounds are formed from the type $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, by the substitution of a positive and a negative radical for the two atoms of hydrogen: Thus, monobasic sulpharseniate of potassium, $\left.\begin{matrix}As\\K\end{matrix}\right\}S_3$; tribasic sulpharseniate of potassium, $\left.\begin{matrix}AsS\\K_3\end{matrix}\right\}S_3$; these formulæ are evidently analogous to those of the monobasic and tribasic phosphates.

The *compound sulphur-ethers* are sulphur-salts, in which the positive element is an alcohol radical:—For example, sulphocyanide of ethyl, $\left.\begin{matrix}Cy\\C_2H_5\end{matrix}\right\}S$; sulphocyanide of allyl, or oil of mustard, $= \left.\begin{matrix}Cy\\C_3H_5\end{matrix}\right\}S$.

Sulphide of acetyl and ethyl, or thiacetic ether, is obtained by the action of persulphide of phosphorus on acetic acid: —

$$5\left(\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O\right) + P_2S_5 = 5\left(\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}S\right) + P_2O_5.$$

HYDROCHLORIC ACID TYPE.

CHLORIDES.—The *basic metallic chlorides* are, like the oxides, either monatomic or polyatomic; *e. g.* —

$$\underbrace{KCl}_{\text{Monatomic.}} \qquad \underbrace{PtCl_2}_{\text{Biatomic.}} \qquad \underbrace{Fe_2Cl_3 . AuCl_3.}_{\text{Tritaomic.}}$$

The biatomic and triatomic chlorides unite with the monatomic chlorides, forming crystalline compounds, whose composition may be illustrated by the formulæ of—

Chloro-aurate of sodium ....$NaCl.AuCl_3 = \left.\begin{matrix}Na\\Au\end{matrix}\right\}Cl_4$.

Chloroplatinate of ammonium, $NH_4Cl.PtCl_2 = \left.\begin{matrix}NH_4\\Pt\end{matrix}\right\}Cl_3$.

The chlorides of gold and platinum form similar compounds with the hydrochlorates of the organic bases, which may be represented by analogous formulæ. Thus, chloroplatinate of ethylamine, $\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\\H\end{matrix}\right\}N.HCl + PtCl_2 = \left.\begin{matrix}NH_3(\text{Ꞓ}_2H_5)\\Pt\end{matrix}\right\}\text{Ꞓ}l_3$.

The hydrochlorate of any organic alkali may be represented as the chloride of a basic radical containing an additional atom of hydrogen, just as sal-ammoniac may be represented either as $NH_3.HCl$, or as NH_4Cl. Thus, hydrochlorate of ethylamine, $NH_2(\text{Ꞓ}_2H_5).HCl = NH_3(\text{Ꞓ}_2H_5).Cl$.

The *chlorides of the alcohol-radicals*, or *hydrochloric ethers*, are obtained either by the action of hydrochloric acid, or one of the chlorides of phosphorus, on the alcohols:—

$$\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{Ɵ} + HCl = \left.\begin{matrix}H\\H\end{matrix}\right\}\text{Ɵ} + \text{Ꞓ}_2H_5.Cl.$$

$$\underbrace{3\left(\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{Ɵ}\right)}_{\text{Alcohol.}} + PCl_3 = \underbrace{\left.\begin{matrix}P\\H_3\end{matrix}\right\}\text{Ɵ}_3}_{\text{Phosphorous acid.}} + 3(\underbrace{\text{Ꞓ}_2H_5.Cl}_{\text{Chloride of ethyl.}}).$$

These chlorides are more volatile than the corresponding alcohols.

The *acid*, or *negative chlorides*, are also monatomic, biatomic, or triatomic, according to the acids from which they are derived.

The monatomic chlorides, derived from one atom of hydrochloric acid, contain, in two vapour-volumes, one atom of chlorine, capable of forming a metallic chloride with mineral alkalies; e. g., chloride of cyanogen, $\text{Ꞓ}NCl = Cy.Cl$; chloride of acetyl, $= \text{Ꞓ}_2H_3\text{Ɵ}.Cl$. They are obtained by the action of one of the chlorides of phosphorus on the acids, thus:—

$$\left.\begin{matrix}\text{Ꞓ}_2H_3\text{Ɵ}\\H\end{matrix}\right\}\text{Ɵ} + \underbrace{PCl_2\,.\,Cl_3}_{\text{Perchloride of phosphorus.}} = \underbrace{\frac{\text{Ꞓ}_2H_3\text{Ɵ}\,.\,Cl}{HCl}}_{\text{Chloride of acetyl + hydrochloric acid.}} + \underbrace{P\text{Ɵ}.Cl_3}_{\text{Oxychloride of phosphorus.}}$$

$$3\left(\left.\begin{matrix}\text{Ꞓ}_2H_3\text{Ɵ}\\H\end{matrix}\right\}\text{Ɵ}\right) + PCl_3 = \left.\begin{matrix}P\\H_3\end{matrix}\right\}\text{Ɵ}_3 + 3(\text{Ꞓ}_2H_3\text{Ɵ}.Cl.)$$

Or, by the action of oxychloride of phosphorus on an alkaline salt of the same acid:—

$$\left(\left.\begin{matrix}\text{Ꞓ}_2H_3\text{Ɵ}\\K\end{matrix}\right\}\text{Ɵ}\right) + P\text{Ɵ}.Cl_3 = \left.\begin{matrix}P\text{Ɵ}\\K_3\end{matrix}\right\}\text{Ɵ}_3 + 3(\text{Ꞓ}_2H_3\text{Ɵ}.Cl.)$$

The biatomic chlorides, derived from two molecules of hydrochloric acid, contain, within two vapour-volumes, two atoms of chlorine, capable of forming a metallic chloride with alkalies:—

Chloride of carbonyl, oxychloride of carbon, or phosgene...... $= \text{ꞒƟ}.Cl_2$
Chloride of sulphuryl.. $= \text{ꞨƟ}_2.Cl_2$
Chloride of succinyl .... $= \text{Ꞓ}_4H_4\text{Ɵ}_4.Cl_2$
Chloride of chromyl, or chlorochromic acid.......................... $= Cr_2\text{Ɵ}_2.Cl_2$

These chlorides may be obtained by the action of pentachloride of phosphorus upon the corresponding anhydrous acids.

The action of pentachloride of phosphorus on a bibasic acid is supposed by Gerhardt to consist of two stages,—the first being the formation of an anhydrous acid, the second the conversion of that compound into a chloride. For example:—

$$\left.\begin{matrix}\mathrm{Ȼ_4H_4Θ_2.Θ}\\\mathrm{H_2.Θ}\end{matrix}\right\} + \mathrm{PCl_2.Cl_3} = \mathrm{Ȼ_4H_4Θ_2.Θ} + \mathrm{2HCl} + \mathrm{PΘCl_3};$$

and $\mathrm{Ȼ_4H_4Θ_2.Θ} + \mathrm{PCl_2.Cl_3} = \mathrm{Ȼ_4H_4Θ_2.Cl_2} + \mathrm{PΘCl_3}$;

whereas, in the case of a monobasic acid, the action consists of one stage only. This difference is connected by Gerhardt with the fact, that a bibasic acid may be supposed to contain water, whereas a monobasic acid cannot (p. 704). According to Williamson. on the contrary, the two stages of the reaction, in the case of a bibasic acid, are precisely similar to one another, and to the single reaction which takes place with monobasic acids. Thus, with sulphuric acid—

$$\left.\begin{matrix}\mathrm{SΘ_2}\\\mathrm{H_2}\end{matrix}\right\}\mathrm{Θ_2} + \mathrm{PCl_2.Cl_3} = \left.\begin{matrix}\mathrm{SΘ_2}\\\mathrm{HCl}\end{matrix}\right\}\mathrm{Θ} + \mathrm{HCl} + \mathrm{PΘCl_3},$$

and $\left.\begin{matrix}\mathrm{SΘ_2}\\\mathrm{HCl}\end{matrix}\right\}\mathrm{Θ} + \mathrm{PCl_2.Cl_3} = \mathrm{SΘ_2.Cl_2} + \mathrm{HCl} + \mathrm{PΘCl_3}$.

The difference in the two views of the reaction is this:—that the former supposes the first stage of the action to consist in the formation of an anhydrous acid; the second supposes an intermediate compound,—a chloro-hydrate of the acid, to be produced. The formation of this chloro-hydrate has been shown by Professor Williamson to take place with sulphuric acid. If, however, one of the two molecules of hydrochloric acid in Gerhardt's first equation be supposed to remain associated with the anhydrous acid, the two views will nearly coincide. In every case, indeed, the reaction consists essentially in the interchange of $\mathrm{Θ}$ and $\mathrm{Cl_2}$.

The triatomic chlorides, or terchlorides, contain, within two vapour-volumes, three atoms of chlorine capable of forming a metallic chlorine when acted upon by the mineral alkalies.

The following acid chlorides are triatomic:—

Terchloride of phosphorus	$\mathrm{P.Cl_3}$.
Chloride of phosphoryl (oxychloride of phosphorus)	$\mathrm{PΘ{\cdot}Cl_3}$.
Chloride of sulphophosphoryl (sulphochloride of phosphorus)	$\mathrm{PS.Cl_3}$.
Chloride of chlorophosphoryl (pentachloride of phosphorus)	$\mathrm{PCl_2.Cl_3}$.
Chloride of boron	$\mathrm{B.Cl_3}$.
Chloride of cyanuryl (solid chloride of cyanogen)	$\mathrm{Cy_3.Cl_3}$.

The BROMIDES, IODIDES, and FLUORIDES, are exactly analogous to the chlorides. There are very few organic fluorides known.

The CYANIDES are also analogous to the chlorides.

The *metallic cyanides* have a great tendency to unite and form double cyanides, which may be regarded as derivatives of two or more atoms of hydrochloric acid. Thus, the *ferrocyanides* may be represented by the formula $\left.\begin{matrix}\mathrm{Fe}\\\mathrm{M_2}\end{matrix}\right\}\mathrm{Cy_3}$, and the *ferricyanides*, by $\left.\begin{matrix}\mathrm{M_3}\\\mathrm{Fe_2}\end{matrix}\right\}\mathrm{Cy_6}$; the $\mathrm{Fe_2}$ in the latter formula being equivalent to $\mathrm{H_3}$.

The *cyanides of the alcohol-radicals* are obtained by distilling a sulphovinate or homologous salt with cyanide of potassium: thus,—

$$\left.\begin{matrix}\mathrm{SΘ_2}\\\mathrm{K.Ȼ_2H_5}\end{matrix}\right\}{}_2\mathrm{Θ} + \mathrm{KCy} = \left.\begin{matrix}\mathrm{SΘ_2}\\\mathrm{K_2}\end{matrix}\right\}\mathrm{Θ_2} + \mathrm{Ȼ_2H_5.Cy};$$

or by the action of anhydrous phosphoric acid on the ammoniacal salts of the fatty acids, the action of the phosphoric acid consisting in the abstraction of water: thus,—

$$\underbrace{\left.\begin{matrix}\mathrm{Ȼ_2H_3Θ}\\\mathrm{NH_4}\end{matrix}\right\}\mathrm{Θ}}_{\text{Acetate of ammonia.}} - \mathrm{2H_2Θ} = \underbrace{\mathrm{ȻN.ȻH_3}}_{\text{Cyanide of methyl.}};$$

or, generally,

$$\left.\begin{matrix}\mathrm{Ȼ_nH_{2n-1}Θ}\\\mathrm{NH_4}\end{matrix}\right\}\mathrm{Θ} - \mathrm{2H_2Θ} = \mathrm{ȻN.Ȼ_{n-1}H_{2n-1}}.$$

The ammonia-salt of each acid in the series yields when thus treated, the cyanide, not of the corresponding alcohol-radical, but of the next lowest; thus: the propionate yields cyanide of ethyl; the acetate, cyanide of methyl; and the formiate, cyanide of hydrogen, or hydrocyanic acid.

When these cyanides are heated with caustic alkalies, the opposite change takes place; that is to say, an alkaline salt of the acid corresponding to the next highest alcohol is formed, and ammonia is evolved: thus, —

$$\underbrace{\text{Ꞓ}NH}_{\substack{\text{Cyanide}\\\text{of hy-}\\\text{drogen.}}} + \left.\begin{matrix}H\\K\end{matrix}\right\}\Theta + H_2\Theta + \underbrace{\left.\begin{matrix}\text{Ꞓ}H\Theta\\K\end{matrix}\right\}\Theta}_{\substack{\text{Formiate of}\\\text{potash.}}} + NH_3;$$

$$\underbrace{\text{Ꞓ}N.\text{Ꞓ}H_3}_{\substack{\text{Cyanide of}\\\text{methyl.}}} + \left.\begin{matrix}H\\K\end{matrix}\right\}\Theta + H_2\Theta = \underbrace{\left.\begin{matrix}\text{Ꞓ}_2H_3\Theta\\K\end{matrix}\right\}\Theta}_{\substack{\text{Acetate of}\\\text{potash.}}} + NH_3;$$

$$\text{Ꞓ}N.\text{Ꞓ}_nH_{2n+1} + \left.\begin{matrix}H\\K\end{matrix}\right\}\Theta + H_2\Theta = \left.\begin{matrix}\text{Ꞓ}_{n+1}H_{2n+1}\Theta\\K\end{matrix}\right\}\Theta + NH_3.$$

These alcoholic cyanides may also be regarded as nitriles: thus, —

$$\underbrace{\text{Ꞓ}NH}_{\substack{\text{Cyanide}\\\text{of hy-}\\\text{drogen.}}} = \underbrace{N.\text{Ꞓ}H}_{\substack{\text{Formo-}\\\text{nitrile.}}};\qquad \underbrace{\text{Ꞓ}N.CH_3}_{\substack{\text{Cyanide of}\\\text{methyl.}}} = \underbrace{N.\text{Ꞓ}_2H_3}_{\substack{\text{Aceto-}\\\text{nitrile.}}};$$

generally: $\text{Ꞓ}N.\text{Ꞓ}_nH_{2n+1} = N.\text{Ꞓ}_{n+1}H_{2n+1}$.

AMMONIA TYPE.

NITRIDES.—*a. Positive.*—These compounds are chiefly organic, constituting in fact the organic bases or alkaloids. A few mineral nitrides have, however, been obtained by the action of ammonia on the metals or their oxides; *e.g.*, amide of potassium, $N(H_2K)$; nitride of potassium, NK_3; nitride of mercury, NHg_3.

The primary nitrides of the alcohol-radicals, such as methylamine, $\text{Ꞓ}H_5N = N(\text{Ꞓ}H_3.H_2)$, amylamine, $\text{Ꞓ}_5H_{13}N = N(\text{Ꞓ}_5H_{11}.H_2)$, are obtained: — 1. By the action of the bromides or iodides of the alcohol-radicals on ammonia: —

$$NH_3 + \underbrace{\text{Ꞓ}_2H_5I}_{\text{Iodide of ethyl.}} = HI + \underbrace{N\left\}\begin{matrix}\text{Ꞓ}_2H_5\\H.\\H\end{matrix}\right.}_{\text{Ethylamine.}}$$

2. By the action of potash on the cyanates or cyanurates of the same radicals: —

$$\underbrace{N\left\{\begin{matrix}\text{Ꞓ}\Theta\\\text{Ꞓ}_2H_5\end{matrix}\right.}_{\substack{\text{Cyanate of}\\\text{ethyl.}}} + \underbrace{\left.\begin{matrix}H_2\\K_2\end{matrix}\right\}\Theta_2}_{\substack{\text{Hydrate of}\\\text{potash.}}} = \underbrace{\left.\begin{matrix}\text{Ꞓ}\Theta\\K_2\end{matrix}\right\}\Theta_2}_{\substack{\text{Carbonate of}\\\text{potash.}}} + \underbrace{N\left\{\begin{matrix}\text{Ꞓ}_2\\H\\H\end{matrix}\right.}_{\text{Ethylamine.}}$$

3. By the action of reducing agents, such as hydrosulphuric acid, or acetate of iron, or certain nitro-conjugated hydrocarbons; thus: —

$$\underbrace{Ꞓ_6H_5(NΘ_2)}_{\text{Nitrobenzol.}} + 3H_2S = \underbrace{N\left\{\begin{matrix}Ꞓ_6H_5\\H\\H\end{matrix}\right.}_{\text{Aniline or phenylamine.}} + 2H_2Θ + 3S.$$

They are also frequently produced in the destructive distillation of nitrogenized organic substances, and are consequently found in coal-tar, bone-oil, &c.

These bodies are all volatile liquids, having more or less of an ammoniacal odour. The bases of the same series — for instance, those formed from the alcohol-radicals $Ꞓ_nH_{2n+1}$—are less volatile and more oily, as they contain more carbon. They all combine with acids in the same manner as ammonia, and form crystallizable double salts with bichloride of platinum. Nitrous acid converts them into alcohols or nitrous ethers, with elimination of nitrogen: —

$$\underbrace{\left.\begin{matrix}Ꞓ_2H_5\\H\\H\end{matrix}\right\}N}_{\text{Ethylamine.}} + \underbrace{\left.\begin{matrix}N\\N\end{matrix}\right\}Θ_3}_{\text{Nitrous acid.}} = NN + \underbrace{\left.\begin{matrix}Ꞓ_2H_5\\N\end{matrix}\right\}Θ_2}_{\text{Nitrite of ethyl.}} + H_2Θ;$$

$$2\left(\underbrace{\left.\begin{matrix}Ꞓ_6H_5\\H\\H\end{matrix}\right\}N}_{\text{Aniline.}}\right) + \left.\begin{matrix}N\\N\end{matrix}\right\}Θ_3 = 2\,NN + \underbrace{2\left(\left.\begin{matrix}Ꞓ_6H_5\\H\end{matrix}\right\}Θ\right)}_{\text{2 mol. hydrate of phenyl.}} + H_2Θ.$$

Secondary alcoholic nitrides.—The constitution of these bodies may be understood from the following examples: —

Biethylamine, $Ꞓ_4H_{11}N$ .... = $\left.\begin{matrix}Ꞓ_2H_5\\Ꞓ_2H_5\\H\end{matrix}\right\}N.$

Metethylamine, $Ꞓ_3H_9N$ .... = $\left.\begin{matrix}Ꞓ_2H_5\\ꞒH_3\\H\end{matrix}\right\}N.$

Ethaniline, or ethyphenylamine, $Ꞓ_8H_{11}N$ .... = $\left.\begin{matrix}Ꞓ_2H_5\\Ꞓ_6H_5\\H\end{matrix}\right\}N.$

They are obtained by the action of the bromides or iodides of the alcohol-radicals on the primary nitrides: —

$$\left.\begin{matrix}Ꞓ_2H_5\\H\\H\end{matrix}\right\}N + Ꞓ_2H_3Br = \left.\begin{matrix}Ꞓ_2H_3\\Ꞓ_2H_5\\H\end{matrix}\right\}N + HBr.$$

Tertiary alcoholic nitrides, or *nitrile bases:* —

Triethylamine, $Ꞓ_6H_{15}N = \left.\begin{matrix}Ꞓ_2H_5\\Ꞓ_2H_5\\Ꞓ_2H_5\end{matrix}\right\}N.$

Biethamylamine, $C_9H_{21}N = \left.\begin{matrix}Ꞓ_2H_5\\Ꞓ_2H_5\\Ꞓ_5H_{11}\end{matrix}\right\}N.$

Methamylaniline, $Ꞓ_{12}H_{19}N = \left.\begin{matrix}ꞒH_3\\Ꞓ_5H_{11}\\Ꞓ_6H_5\end{matrix}\right\}N.$

These compounds are formed by the action of the iodides and bromides of the alcohol-radicals on the secondary alcoholic nitrides; also by the distillation of the ammonium-bases, thus:—

$$\underbrace{\left.\begin{matrix}N(\text{Ꞓ}_2H_5)_4\\ H\end{matrix}\right\}\text{Ɵ}}_{\text{Hydrate of tetrethylium.}} = \underbrace{(\text{Ꞓ}_2H_5)_3N}_{\text{Triethylamine.}} + \underbrace{\text{Ꞓ}_2H_4}_{\text{Ethylene.}} + H_2\text{Ɵ}.$$

Triethylamine is likewise obtained by the action of ethylate of potassium on cyanate of ethyl:—

$$\underbrace{N\left\{\begin{matrix}\text{ꞒƟ}\\ \text{Ꞓ}_2H_5\end{matrix}\right.}_{\text{Cynate of ethyl.}} + \underbrace{\left.\begin{matrix}(\text{Ꞓ}_2H_5)_2\\ K_2\end{matrix}\right\}\text{Ɵ}_2}_{\text{2 at. ethylate of potassium.}} = \underbrace{\left.\begin{matrix}\text{ꞒƟ}\\ K_2\end{matrix}\right\}\text{Ɵ}_2}_{\text{Carbonate of potash.}} + \underbrace{N(\text{Ꞓ}_2H_5)_3.}_{\text{Triethylamine.}}$$

This action is analogous to that of hydrate of potash or cyanate of ethyl (p. 710). The other tertiary alcoholic nitrides might doubtless be obtained in a similar manner.

There are also nitrides containing conjugated alcohol-radicals; *e. g.*:—

Bichlorethylamine........................ $\text{Ꞓ}_2H_5Cl_2N = \left.\begin{matrix}\text{Ꞓ}_2H_3Cl_2\\ H\\ H\end{matrix}\right\}N.$

Chloraniline.............................. $\text{Ꞓ}_9H_6ClN = \left.\begin{matrix}\text{Ꞓ}_6H_4Cl\\ H\\ H\end{matrix}\right\}N.$

Nitraniline.............................. $\text{Ꞓ}_6H_6(NO_2)N = \left.\begin{matrix}\text{Ꞓ}_6H_4(N\text{Ɵ}_2)\\ H\\ H\end{matrix}\right\}N.$

Nitrides of aldehyde-radicals.—These bodies are but little known.

Acetosylamine, $N(H_2 . \text{Ꞓ}_2H_3)$, is obtained by the action of ammonia on chloride of ethylene (chloride of acetosyl and hydrogen):—

$$\underbrace{\left.\begin{matrix}\text{Ꞓ}_2H_3\\ H\end{matrix}\right\}Cl_2}_{\text{Chloride of acetosyl and hydrogen.}} + 2NH_3 = \underbrace{\left.\begin{matrix}\text{Ꞓ}_2H_3\\ H\\ H\end{matrix}\right\}N . HCl}_{\text{Hydrochlorate of acetosylamine.}} + NH_4Cl.$$

The natural vegeto-alkalies, morphine, strychnine, &c., are most probably of similar nature to these artificial alkalies, but they have not yet been reduced to regular series.

b. Negative or *acid nitrides.*—These are the compounds generally called *amides.*

Primary amides.—In these compounds, one-third of the hydrogen in 1, 2, or 3 molecules of ammonia is replaced by an acid radical.

a. Monatomic:—

Acetamide, or nitride of acetyl and hydrogen .... $\text{Ꞓ}_2H_5N\text{Ɵ} = N\left\{\begin{matrix}\text{Ꞓ}_2H_3\text{Ɵ}\\ H\\ H\end{matrix}\right..$

Butyramide, or nitride of butyryl and hydrogen....... $C_4H_9NO = N\left\{\begin{matrix}C_4H_7O\\ H\\ H\end{matrix}\right.$.

Benzamide, or nitride of benzoyl and hydrogen........ $C_7H_7NO = N\left\{\begin{matrix}C_7H_5O\\ H\\ H\end{matrix}\right.$.

These amides differ from the corresponding ammoniacal salts by the elements of one atom of water:—

$$\underbrace{\left.\begin{matrix}C_2H_3O\\ NH_4\end{matrix}\right\}O}_{\text{Acetate of ammonia.}} - H_2O = \underbrace{N\left\{\begin{matrix}C_2H_3O\\ H_2\end{matrix}\right.}_{\text{Acetamide.}}.$$

They are produced by the action of ammonia on the anhydrous acids:—

$$\underbrace{\left.\begin{matrix}C_7H_5O\\ C_7H_5O\end{matrix}\right\}O}_{\text{Benzoic anhydride.}} + NH_3 = \underbrace{\left.\begin{matrix}C_7H_5O\\ H\end{matrix}\right\}O}_{\text{Benzoic acid.}} + \underbrace{N\left\{\begin{matrix}C_7H_5O\\ H_2\end{matrix}\right.}_{\text{Benzamide.}};$$

by the action of ammonia on the acid chlorides:—

$$C_7H_5O.Cl + NH_3 = HCl + N\left\{\begin{matrix}C_7H_5O\\ H_2\end{matrix}\right.;$$

and by the action of ammonia on the compound ethers:—

$$\underbrace{\left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O}_{\text{Acetate of ethyl.}} + NH_3 = \underbrace{\left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}O}_{\text{Alcohol.}} + \underbrace{N\left\{\begin{matrix}C_2H_3O\\ H\\ H\end{matrix}\right.}_{\text{Acetamide.}}.$$

These amides are neutral crystalline bodies, which, when boiled with aqueous acids or alkalies, take up water, and are converted into ammonia-salts. When treated with anhydrous phosphoric acid, they give up the elements of 1 at. water, and are converted into cyanides of the alcohol radicals:—

$$\underbrace{N\left\{\begin{matrix}C_2H_3O\\ H_2\end{matrix}\right.}_{\text{Acetamide.}} - H_2O = \underbrace{CN.CH_3}_{\text{Cyanide of methyl.}}.$$

β. Biatomic. *Primary biamides* or *diamides*:—

Oxamide, or nitride of oxalyl and hydrogen......... $C_2H_4N_2O_2 = N_2\left\{\begin{matrix}C_2O_2\\ H_2\\ H_2\end{matrix}\right.$.

Succinamide, or nitride of succinyl and hydrogen... $C_4H_8N_2O_2 = N_2\left\{\begin{matrix}C_4H_4O_2\\ H_2\\ H_2\end{matrix}\right.$.

Urea and carbamide, or nitride of carbonyl and hydrogen .... $\Big\}\ CH_4N_2O = N_2\left\{\begin{matrix}CO\\ H_2\\ H_2\end{matrix}\right.$.

Tartramide, or nitride of tartryl and hydrogen...... $C_4H_8N_2O_4 = N_2\left\{\begin{matrix}C_4H_4O_4\\ H_2\\ H_2\end{matrix}\right.$.

They are produced by the action of heat on the neutral ammonia-salts of bibasic acids:—

$$\underbrace{\left.\begin{matrix}\text{Ꞓ}_2\text{Ɵ}_2\\(\text{NH}_4)_2\end{matrix}\right\}}_{\text{Oxalate of ammonia.}}\text{Ɵ}_2 - 2\text{H}_2\text{Ɵ} = \underbrace{\text{N}_2\left\{\begin{matrix}\text{Ꞓ}_2\text{Ɵ}_2\\\text{H}_2;\\\text{H}_2\end{matrix}\right.}_{\text{Oxamide.}}$$

by the combination of ammonia with secondary amides :—

$$\underbrace{\text{N}\left\{\begin{matrix}\text{ꞒƟ}\\\text{H}\end{matrix}\right.}_{\text{Cyanic acid, or carbonimide.}} + \text{NH}_3 = \underbrace{\text{N}_2\left\{\begin{matrix}\text{ꞒƟ}\\\text{H}_2;\\\text{H}_2\end{matrix}\right.}_{\text{Urea.}}$$

and by the action of ammonia on compound ethers or acid chlorides :—

$$\underbrace{\left.\begin{matrix}\text{Ꞓ}_2\text{Ɵ}_2\\(\text{Ꞓ}_2\text{H}_5)_2\end{matrix}\right\}\text{Ɵ}_2}_{\text{Oxalate of ethyl.}} + 2\text{NH}_3 = \underbrace{\left.\begin{matrix}\text{H}_2\\(\text{Ꞓ}_2\text{H}_5)_2\end{matrix}\right\}\text{Ɵ}_2}_{\text{2 at. alcohol.}} + \underbrace{\text{N}_2\left\{\begin{matrix}\text{Ꞓ}_2\text{Ɵ}_2\\\text{H}_4\end{matrix}\right.}_{\text{Oxamide.}}.$$

$$\underbrace{\text{Ꞓ}_4\text{H}_4\text{Ɵ}_2.\text{Cl}_2}_{\text{Chloride of succinyl.}} + 2\text{NH}_3 = 2\text{HCl} + \underbrace{\text{N}_2\left\{\begin{matrix}\text{Ꞓ}_4\text{H}_4\text{Ɵ}_2\\\text{H}_4\end{matrix}\right.}_{\text{Succinamide.}}.$$

γ.—Triatomic. *Primary triamides :—*

Triphosphamide, or nitride of phosphoryl and hydrogen............$\text{N}_3\left\{\begin{matrix}\text{PƟ}\\\text{H}_6\end{matrix}\right.$.

Citramide, or nitride of citryl and hydrogen.........$\text{Ꞓ}_6\text{H}_{11}\text{N}_3\text{Ɵ}_4 = \text{N}^3\left\{\begin{matrix}\text{Ꞓ}_6\text{H}_5\text{Ɵ}_4\\\text{H}_6\end{matrix}\right.$.

Melamine and melam, or nitride of cyanuryl and hydrogen ....} $\text{Ꞓ}_3\text{H}_6\text{N}_6 = \text{N}_3\left\{\begin{matrix}\text{Cy}_3\\\text{H}_6\end{matrix}\right.$.

Secondary amides.—In these compounds, two-thirds of the hydrogen in a molecule of ammonia are replaced by acid radicals, viz. :

1. By two monatomic radicals; *e. g.* :—

Nitride of bisulphophenyl and hydrogen ... .$\text{Ꞓ}_{12}\text{H}_{11}\text{NꞨ}_2\text{Ɵ}_4 = \text{N}\left\{\begin{matrix}\text{Ꞓ}_6\text{H}_5\text{ꞨƟ}_2\\\text{Ꞓ}_6\text{H}_5\text{ꞨƟ}_2\\\text{H}\end{matrix}\right.$.

Nitride of sulphophenyl, benzoyl and hydrogen...$\text{Ꞓ}_{13}\text{H}_{11}\text{NꞨ}_2\text{Ɵ}_4 = \text{N}\left\{\begin{matrix}\text{Ꞓ}_6\text{H}_5\text{ꞨƟ}_2\\\text{Ꞓ}_7\text{H}_5\text{Ɵ}\\\text{H}\end{matrix}\right.$.

These amides are produced by the action of acid chlorides on the primary amides or their metallic salts.

$$\text{N}\left\{\begin{matrix}\text{Ꞓ}_6\text{H}_5\text{ꞨƟ}_2\\\text{H}\\\text{H}\end{matrix}\right. + \text{C}_7\text{H}_5\text{Ɵ.Cl} = \text{N}\left\{\begin{matrix}\text{Ꞓ}_6\text{H ꞨƟ}_2\\\text{Ꞓ}_7\text{H}_5\text{Ɵ}\\\text{H}\end{matrix}\right. + \text{HCl}.$$

2. The two atoms of hydrogen are replaced by one molecule of a biatomic radical. These compounds are called *imides.*

Carbonimide (cyanic acid) or nitride of carbonyl and hydrogen ....} $\text{ꞒNHƟ} = \text{N}\left\{\begin{matrix}\text{ꞒƟ}\\\text{H}\end{matrix}\right.$.

Succinimide, or nitride of succinyl and hydrogen ....$\text{Ꞓ}_4\text{H}_5\text{NƟ}_2 = \text{N}\left\{\begin{matrix}\text{Ꞓ}_4\text{H}_4\text{Ɵ}_2\\\text{H}\end{matrix}\right.$.

Most of them are produced by the action of heat on the acid ammoniacal salts of bibasic acids, the change consisting in the elimination of 2 molecules of water:—

$$\underbrace{\left.\begin{matrix}C_4H_4O_2\\H\\NH_4\end{matrix}\right\}}_{\text{Acid succinate of ammonia.}}O_2 - 2H_2O = \underbrace{N\left\{\begin{matrix}C_4H_4O_2\\H\end{matrix}\right.}_{\text{Succinimide.}};$$

by the action of heat on the biamides of bibasic acids, ammonia being then given off:—

$$\underbrace{N_2\left\{\begin{matrix}C_4H_4O_2\\H_2\\H_2\end{matrix}\right.}_{\text{Succinamide.}} - NH_3 = \underbrace{N\left\{\begin{matrix}C_4H_4O_2\\H\end{matrix}\right.}_{\text{Succinimide.}};$$

or by the action of heat on the amidogen acids.

Tertiary Amides.—In these compounds, all the hydrogen in ammonia is replaced by acid radicals.

α. *Monatomic.*—1. The hydrogen is replaced by three monatomic radicals; *e. g.*:—

Nitride of sulphophenyl, benzoyl, and acetyl........................ $N\left\{\begin{matrix}C_6H_5SO_2\\C_7H_5O\\C_2H_3O\end{matrix}\right.$.

Nitride of sulphophenyl and benzoyl.................................. $N\left\{\begin{matrix}C_6H_5SO_2\\C_7H_5O\\C_7H_5O\end{matrix}\right.$.

2. One atom of hydrogen is replaced by a monatomic, and the other two by a biatomic radical:—

Nitride of succinyl and sulphophenyl.................................. $N\left\{\begin{matrix}C_4H_4O_2\\C_6H_5SO_2\end{matrix}\right.$.

These amides are formed by the action of acid chlorides on the secondary amides, or their silver-salts.

3. All the hydrogen is replaced by a triatomic radical. The composition of several inorganic compounds may be expressed in this manner:—

Monophosphamide, or nitride of phosphoryl.............................. $= N . PO$.
Boramide, or nitride of boron.. $= N . B$.
Free nitrogen, or nitride of nitrogen, the amide of nitrous acid ... $= N . N$.
Protoxide of nitrogen, or nitride of azotyl, the amide of nitric acid $= N . NO$.

β. *Biatomic.*—Compounds in which all the hydrogen of 2 molecules of ammonia is replaced by monatomic or biatomic radicals:—

Trisuccinamide, or biamide of trisuccinyl.......................... $N_2\left\{\begin{matrix}C_4H_4O_2\\C_4H_4O_2\\C_4H_4O_2\end{matrix}\right.$.

Biamide of succinyl, bibenzoyl, and bisulphophenyl .... $N_2\left\{\begin{matrix}C_4H_4O_2\\(C_7H_5O)_2\\(C_6H_5SO_2)_2\end{matrix}\right.$.

These *tertiary biamides* are produced by the action of acid chlorides on other amides or biamides.

Intermediate nitrides, or *amidogen-salts.*—These are compounds in which the hydrogen of ammonia is replaced partly by a basic, partly by an acid radical. Most of the primary and secondary amides form such salts, which are produced by the direct action of the amides on the corresponding oxides or their salts; *e.g.*:—

Benzamidate of mercury .... $N\left\{\begin{matrix}C_7H_5O\\ Hg.\\ H\end{matrix}\right.$

When the positive radical is an alcohol-radical, the compounds are called *alcalamides;* those which contain phenyl, C_6H_5, are also called anilides: thus,—

Phenyl-acetamide or acetanilide .... $N\left\{\begin{matrix}C_6H_5\\ C_2H_3O.\\ H\end{matrix}\right.$

Ethyl-cyanamide .... $N\left\{\begin{matrix}C_2H_5\\ Cy.\\ H\end{matrix}\right.$

PHOSPHIDES.—These compounds are derived from the type ammonia by the substitution of phosphorus for nitrogen, and of various radicals for the hydrogen. Phosphuretted hydrogen, PH_3, is analogous to ammonia, and forms with hydriodic acid a compound, $PH_3 . HI$, or PH_4I, which crystallizes in cubes like iodide of ammonium, or iodide of potassium.

With the alcohol-radicals, phosphorus forms compounds analogous to the alcoholic nitrides, and like those bodies possessing alkaline properties; *e.g.*, triphosphomethylamine, or trimethyphosphine, $P(CH_3)_3$. These compounds may be obtained by the action of terchloride of phosphorus on zinc-methyl, zinc-ethyl, &c., the reaction being expressed by the following general equation:—

$$PCl_3 + 3C_nH_{2n+1}Zn = 3ZnCl + P(C_nH_{2n+1})_3.$$

These phosphides, treated with the iodides of the corresponding alcohol-radicals, yield compounds analogous to the ammonium bases: thus,—

$$P(CH_3)_3 + C_2H_5I = \left.\begin{matrix}(CH_3)_3\\ C_2H_5\end{matrix}\right\}P\,.\,I.$$

The only negative or acid phosphide known is chloracetyphide, or phosphide of terchloracetyl $= P(C_2Cl_3O . H . H)$.

ARSENIDES AND ANTIMONIDES.—Arsenic and antimony also form compounds of the ammonia type; *e.g.*, AsH_3; SbH_3; $As(C_2H_5)_3$; $Sb(C_2H_5)$; but the arsenides and antimonides of the alcohol-radicals differ considerably in their properties from the nitrides and phosphides, not combining with hydrochloric acid, &c., in the same manner as ammonia, but rather combining with oxygen, chlorine, iodine, &c., like metals. They belong, therefore, rather to the hydrogen type (p. 719).

HYDROGEN TYPE.

The primary derivatives of this type are:—

1. The *hydrides of the metals proper.* A small number only of these are known, viz., Cu_2H, AsH_3, and SbH_3. The two latter may also be regarded as derivatives of ammonia.

2. The *hydrides of the alcohol-radicals,* C_nH_{2n+1}, viz., marsh-gas, or hydride of methyl, $CH_4 = H . CH_3$; hydride of ethyl, $C_2H_6 = H . C_2H_5$; hydride of amyl, $C_5H_{12} = H . C_5H_{11}$, &c. These compounds are formed by the action of zinc on the chlorides or iodides of the corresponding alcohol-radicals:—

$$\underbrace{2C_2H_5I}_{\substack{\text{Iodide of}\\ \text{ethyl.}}} + Zn\;Zn = 2ZnI + \underbrace{H . C_2H_5}_{\substack{\text{Hydride of}\\ \text{ethyl.}}} + \underbrace{C_2H_4}_{\text{Ethylene.}};$$

also by the action of water on zinc-methyl, zinc-ethyl, &c.:—

$$\mathrm{Zn}\,.\,\text{Ꞓ}_2\mathrm{H}_5 + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\text{Ɵ} = \mathrm{H}\,.\,\text{Ꞓ}_2\mathrm{H}_5 + \left.\begin{matrix}\mathrm{Zn}\\\mathrm{H}\end{matrix}\right\}\text{Ɵ};$$

occasionally also in the destructive distillation or spontaneous decomposition of vegetable and animal substances. Marsh-gas, for example, is formed by the putrefaction of vegetable matter under water (p. 278). The hydrides of methyl and ethyl are gaseous at ordinary temperatures, the rest are liquid or solid. They are decomposed by chlorine, with formation of substitution-products; thus—

$$\mathrm{H}\,.\,\text{Ꞓ}_2\mathrm{H}_5 + \mathrm{ClCl} = \mathrm{H}\,.\,\text{Ꞓ}_2(\mathrm{H}_4\mathrm{Cl}) + \mathrm{HCl}.$$

There are likewise hydrides of alcohol-radicals of the form $\mathrm{H}\,.\,\text{Ꞓ}_n\mathrm{H}_{2n-7}$, the best known of which is benzol, or hydride of phenyl, $\text{Ꞓ}_6\mathrm{H}_6$, or $\mathrm{H}\,.\,\text{Ꞓ}_6\mathrm{H}_5$. These compounds are obtained in the destructive distillation of many organic substances; benzol, for instance, by the distillation of coal. They are also formed by the dry distillation of the monobasic acids, $\text{Ꞓ}_n\mathrm{H}_{2n-9}\text{Ɵ}$, with excess of lime or baryta, a carbonate of the base being formed at the same time:—

$$\underbrace{\text{Ꞓ}_7\mathrm{H}_6\text{Ɵ}_2}_{\text{Benzoic acid.}} = \text{ꞒƟ}_2 + \underbrace{\text{Ꞓ}_6\mathrm{H}_6}_{\text{Benzol.}}.$$

3. The *hydrides of the aldehyde-radicals*, $\text{Ꞓ}_n\,\mathrm{H}_{2n-1}$. These are:—

Ethylene, olefiant gas, or hydride of acetosyl .... $\text{Ꞓ}_2\mathrm{H}_4 = \mathrm{H}\,.\,\text{Ꞓ}_2\mathrm{H}_3$.
Propylene, or hydride of propionyl .... $\text{Ꞓ}_3\mathrm{H}_6 = \mathrm{H}\,.\,\text{Ꞓ}_3\mathrm{H}_5$.
Butylene, or hydride of butyryl .... $\text{Ꞓ}_4\mathrm{H}_8 = \mathrm{H}\,.\,\text{Ꞓ}_4\mathrm{H}_7$.
Amylene, or hydride of valeryl .... $\text{Ꞓ}_5\mathrm{H}_{10} = \mathrm{H}\,.\,\text{Ꞓ}_5\mathrm{H}_9$.

These compounds might also be regarded as hydrides of the alcohol-radicals, $\text{Ꞓ}_n\,\mathrm{H}_{2n-1}$; for example, propylene as hydride of allyl (p. 698). Possibly, however, there may be two isomeric series of these compounds, the one derived from the alcohols, the other from the aldehydes.

These hydro-carbons are formed by the destructive distillation of organic substances, several of them being found among the products of the distillation of coal. They are also produced by the action of strong sulphuric acid at a high temperature on the alcohols, the change consisting in the abstraction of the elements of water: thus:—

$$\underbrace{\text{Ꞓ}_2\mathrm{H}_6\text{Ɵ}}_{\text{Alcohol.}} - \mathrm{H}_2\text{Ɵ} = \underbrace{\text{Ꞓ}_2\mathrm{H}_4}_{\text{Ethylene.}}.$$

The only body of the series which is gaseous at ordinary temperatures is ethylene (p. 285); the rest are liquid or solid. The first term, methylene, has not been obtained in the free state. These compounds are especially distinguished by combining with two atoms of chlorine, bromine, &c., forming compounds homologous with Dutch liquid or chloride of ethylene, $\text{Ꞓ}_2\mathrm{H}_4\,.\,\mathrm{Cl}_2$; whereas the hydrides of the radicals $\text{Ꞓ}_n\mathrm{H}_{2n+1}$ are decomposed by chlorine.

The lower compounds of the series also combine with anhydrous sulphuric acid. Thus, olefiant gas is immediately absorbed by the anhydrous acid, or by a coke ball soaked in fuming oil of vitriol. This property, and that of forming liquid compounds with chlorine and bromine, is made available for separating olefiant gas, and the other more volatile hydrocarbons of the series, from gaseous mixtures.

4. The hydrides of the acid radicals,

a. Monatomic.—The hydrides of the acid radicals $\text{Ꞓ}^n\mathrm{H}_{2n-1}\mathrm{O}$, are evidently the aldehydes of the fatty acids (p. 699): thus:—

Acetic aldehyde	$= H\,.\,\text{Ꞓ}_2H\text{Ɵ}_3 = \left.\begin{matrix}\text{Ꞓ}_2H_3\\H\end{matrix}\right\}\text{Ɵ}.$
Butyric aldehyde	$= H\,.\,\text{Ꞓ}_4H_7\text{Ɵ} = \left.\begin{matrix}\text{Ꞓ}_4H_7\\H\end{matrix}\right\}\text{Ɵ}.$
Benzoic aldehyde (bitter almond oil)	$= H\,.\,\text{Ꞓ}_7H_5\text{Ɵ} = \left.\begin{matrix}\text{Ꞓ}_7H_5O\\H\end{matrix}\right\}\text{Ɵ}.$

The following compounds may be regarded as the aldehydes of monobasic mineral acids; that is to say, as the hydrides of the radicals contained in those acids considered as derivatives of water:—

Nitrous acid, or aldehyde of nitric acid	$NH\text{Ɵ}_2$	$= H\,.\,NO_2.$
Hydrochloric acid, or aldehyde of hypochlorous acid	ClH	$= H\,.\,Cl.$
Hydrocyanic acid, or aldehyde of cyanic acid	$\text{Ꞓ}HN$	$= H\,.\,Cy.$
Spontaneous inflammable phosphuretted hydrogen, or aldehyde of hypophosphorous acid	PH	$= H\,.\,P.$

β. Hydrides of biatomic acid radicals:—

Hydrosulphuric acid, or aldehyde of hyposulphurous acid	$\text{Ꞩ}H_2$	$= H_2\,.\,\text{Ꞩ}.$
Hydroselenic acid, or aldehyde of hyposelenious acid	$\text{Ꞩe}H_2$	$= H_2\,.\,\text{Ꞩe}.$

γ. Hydrides of triatomic acid radicals:—

Non-spontaneously inflammable phosphurretted hydrogen, or aldehyde of phosphorous acid	PH_3	$= H_3\,.\,P.$
Antimoniuretted hydrogen, or aldehyde of antimonious acid.	SbH_3	$= H_3\,.\,Sb.$

The secondary derivatives of the hydrogen-type are—

1. The ordinary metals:—Potassium, KK, derived from HH; antimony, SbSb, derived from H_3H_3; aluminium, Al_2Al_2, derived from H_3H_3, &c.

2. The *alcohol-metals*, derived from the type HH, both atoms of hydrogen being replaced by alcohol radicals. The only bodies of this class which have yet been obtained are those containing the radicals Ꞓ_nH_{2n+1}; viz. (*a.*) Those in which the two atoms of hydrogen are replaced by the same radical: *methyl*, $\text{Ꞓ}H_3\,.\,\text{Ꞓ}H_3$; *ethyl*, $\text{Ꞓ}_2H_5\,.\,\text{Ꞓ}_2H_5$; *butyl* or *tetryl*, $\text{Ꞓ}_4H_9\,.\,\text{Ꞓ}_4H_9$; *amyl*, $\text{Ꞓ}_5H_{11}\,.\,\text{Ꞓ}_5H_{11}$; *caproyl* or *hexyl*, $\text{Ꞓ}_6H_{13}\,.\,\text{Ꞓ}_6H_{13}$; and *capryl* or *octyl*, $\text{Ꞓ}_8H_{17}\,.\,\text{Ꞓ}_8H_{17}$.—(*b.*) Those in which the two atoms of hydrogen are replaced by different radicals: *ethylo-butyl, ethyl-amyl, methylo-caproyl, butyl-amyl, and butylo-caproyl.* The reasons for representing the bodies of the class (*a.*) in the free state, by the double formulæ, have been already given (p. 690).

These alcohol-metals are obtained by the action of zinc on the iodides of the alcohol-radicals (p. 697); by the action of sodium on the chlorides of the same radicals; and by the electrolysis of the alkaline salts of the fatty acids, carbonic acid and hydrogen being evolved at the same time:—

$$\underbrace{2\left(\left.\begin{matrix}\text{ꞒƟ}.\text{Ꞓ}H_3\\K\end{matrix}\right\}\text{Ɵ}\right)}_{\text{Acetate of potash.}} + H_2\text{Ɵ} = \underbrace{(\text{Ꞓ}H_3)_2}_{\text{Methyl.}} + H_2 + \text{ꞒƟ}_2 + \underbrace{\left.\begin{matrix}\text{ꞒƟ}\\K_2\end{matrix}\right\}\text{Ɵ}_2}_{\text{Carbonate of Potash.}}.$$

The alcohol-metals, containing two different radicals, are obtained by the action of sodium on a mixture of the corresponding iodides: thus, with the iodides of ethyl and butyl—

$$\text{Ꞓ}_2H_5I + Na\,Na = NaI + Na\text{Ꞓ}_2H_5$$

and

$$\text{Ꞓ}_4H_9I + Na\text{Ꞓ}_2H_5 = NaI + \text{Ꞓ}_2H_5\,.\,\text{Ꞓ}_4H_9;$$

also, by the electrolysis of a mixture of the alkaline salts of two of the fatty acids.

Methyl and ethyl are gaseous at ordinary temperatures; the other alcohol-metals are liquids more or less volatile. They exhibit but little tendency to unite with other bodies. The alcohols and ethers cannot be formed from them directly. Oxygen and sulphur do not act upon them, and chlorine and bromine do not unite with them, but decompose them, forming substitution-products; they are not attacked by hydrochloric acid or by potash. For their boiling points and vapour-densities, see page 690.

3. Mixed metals, containing a metal proper and an alcohol-radical; *e.g. zinc-methyl*, $\text{Ȼ}H_3\,.\,Zn$; *zinc-ethyl*, $\text{Ȼ}_2H_5\,.\,Zn$; *zinc-amyl*, $\text{Ȼ}_5H_{11}Zn$; *stannethyl*, Ȼ_2H_5Sn; *arsenethyl*, $(\text{Ȼ}_2H_5)_3As$; *stibmethyl*, $(\text{Ȼ}H_3)Sb$, &c.

These compounds are obtained by the action of iodide of ethyl, &c., on the corresponding metals, or their alloys with potassium or sodium; thus, the compounds of ethyl and arsenic are obtained by distilling iodide of ethyl with arsenide of sodium; arsen-bimethyl or cacodyl, $(\text{Ȼ}H_3)_2As$, is likewise produced by the dry distillation of a mixture of acetate of soda and arsenious acid. To understand this reaction, it must be remembered that the radical of acetic acid, $\text{Ȼ}_2H_3\Theta$, may be supposed to consist of $\text{Ȼ}\Theta$ conjugated with methyl, $\text{Ȼ}H_3$:—

$$\underbrace{4\left(\left.\begin{matrix}\text{Ȼ}\Theta\,.\,\text{Ȼ}H_3\\ Na\end{matrix}\right\}\Theta\right)}_{\text{Acetate of soda.}} + As_2\Theta_3 = \underbrace{\left.\begin{matrix}(\text{Ȼ}H_3)_2As\\ (\text{Ȼ}H_3)_2As\end{matrix}\right\}}_{\text{Oxide of cacodyl.}}\Theta + 2\text{Ȼ}\Theta_2 + 2\left(\left.\begin{matrix}\text{Ȼ}\Theta\\ Na_2\end{matrix}\right\}\Theta_2\right).$$

These compounds are liquids more or less volatile, and generally having a very offensive odour; they oxidize rapidly in the air, and sometimes take fire. Zinc-methyl, zinc-ethyl, and cacodyl take fire instantly on coming in contact with the air.

Zinc-methyl, zinc-ethyl, and zinc-amyl differ in some respects from the other mixed metals in their behaviour with oxygen, sulphur, chlorine, iodine, &c. When these metals are exposed to the air, but not freely enough to cause them to take fire, they are converted into mixed ethers; thus,—

$$2\,(\text{Ȼ}H_3\,.\,Zn) + \Theta\Theta = 2\left(\left.\begin{matrix}\text{Ȼ}H_3\\ Zn\end{matrix}\right\}\Theta\right).$$

Similarly with sulphur. Chlorine, bromine, and iodine, on the other hand, decompose them, producing a chloride of the metal and a chloride of the alcohol-radical:—

$$\text{Ȼ}H_3\,.\,Zn + ClCl = \text{Ȼ}H_3\,.\,Cl + ZnCl.$$

This difference of reaction is in perfect accordance with the bibasic character of oxygen and sulphur, and the monobasic character of chlorine, bromine, and iodine (compare pp. 689, 707). The same mixed metals decompose water, forming a hydrate of zinc and a hydride of the alcohol-radical:—

$$\text{Ȼ}H_3Zn + \left.\begin{matrix}H\\ H\end{matrix}\right\}\Theta = H\,.\,\text{Ȼ}H_3 + \left.\begin{matrix}Zn\\ H\end{matrix}\right\}\Theta.$$

The other mixed metals—thence called conjugate metals—containing tin, antimony, arsenic, bismuth, lead, and mercury, combine as simple radicals with oxygen, chlorine, &c., forming oxides, chlorides, &c. The oxides of these conjugate metals may be regarded as derivatives of the oxides of the simple metals contained in them, one or more atoms of oxygen being replaced by its equivalent quantity of ethyl, &c.; that is, Θ by $(\text{Ȼ}_2H_5)_2$, &c. This will be seen from the following table, in which the symbol Et stands for $(C_2H_5)_2$:—

Type.	Derivative.	
Arsenious acid, $As_2\Theta_3$.	Oxide of arsen-biethyl	$As_2(Et_2\Theta) = \Theta \left\{ \begin{matrix} As(\text{Ꞓ}_2H_5)_2 \\ As(\text{Ꞓ}_2H_5)_2. \end{matrix} \right.$
Arsenic acid, $As_2\Theta_5$....	Oxide of arsen-triethyl	$As_2(Et_3\Theta_2) = \Theta_2 \left\{ \begin{matrix} As(\text{Ꞓ}_2H_5)_3 \\ As(\text{Ꞓ}_2H_5)_3. \end{matrix} \right.$
Arsenic acid, $As_2\Theta_5$....	Oxide of arsenethylium	$As_2(Et_4\Theta) = \Theta_2 \left\{ \begin{matrix} As(\text{Ꞓ}_2H_5)_4 \\ As(\text{Ꞓ}_2H_5)_4. \end{matrix} \right.$
Stannic oxide, $Sn_2\Theta_2$...	Oxide of stannethyl	$Sn_2(Et\Theta) = \Theta \left\{ \begin{matrix} Sn(\text{Ꞓ}_2H_5) \\ Sn(\text{Ꞓ}_2H_5). \end{matrix} \right.$
Stannic oxide, (2 at.), $Sn_4\Theta_4$	Oxide of $\frac{2}{3}$ stannehyl	$Sn_4(Et_3\Theta) = \Theta_2 \left\{ \begin{matrix} Sn_2(\text{Ꞓ}_2H_5)_3 \\ Sn_2(\text{Ꞓ}_2H_5)_3. \end{matrix} \right.$
Mercuric oxide (at.), $Hg_4\Theta_2$	Oxide of mercurethyl	$Hg_4(Et\Theta) = \Theta_2 \left\{ \begin{matrix} Hg_2(\text{Ꞓ}_2H_5) \\ Hg_2(\text{Ꞓ}_2H_5). \end{matrix} \right.$
Selenious acid (anhy.) (2 at.), $\text{Ꞩ}e_2\Theta_4$.......	Oxide of selenethyl	$\text{Ꞩ}e_2(Et_2\Theta_2) = \Theta_2 \left\{ \begin{matrix} \text{Ꞩ}e(\text{Ꞓ}_2H_5)_2 \\ \text{Ꞩ}e(\text{Ꞓ}_2H_5)_2. \end{matrix} \right.$
Nitric acid (anhyd.), $N_2\Theta_5$	Oxide of tetrethylium	$N_2(Et_1\Theta) = \Theta \left\{ \begin{matrix} N(\text{Ꞓ}_2H_5) \\ N(\text{Ꞓ}_2H_5). \end{matrix} \right.$

The method of determining the equivalent in hydrogen of these conjugate radicals has been already explained (p. 694).

Acid metals, or *metalloids.*—These are the elements commonly called negative or chlorous: *e. g.* oxygen, sulphur, phosphorus, &c.

RELATIONS BETWEEN CHEMICAL COMPOSITION AND DENSITY.

*Atomic Volume of Liquids.**—The atomic volumes of bodies are the spaces occupied by quantities proportional to their atomic weights, and are calculated by dividing the atomic weights by the specific gravities (p. 172); thus, the atomic weights of copper and silver being, on the hydrogen scale, 317 and 108·1, and their specific gravities (water = 1) being 8·93 and 10·57, their atomic volumes are, respectively, $\frac{31\cdot7}{8\cdot93}$ and $\frac{108\cdot1}{10\cdot57}$, or 3·6 and 10·2. These numbers are, of course, only relative; their actual values depend on the units of atomic volume and density adopted.

It has already been observed, that the relations between atomic weight and density are much less simple in solids and liquids than in gases, the diversities in the rates of expansion by heat of liquid and solid bodies being alone sufficient to complicate these relations to a considerable extent. With regard to liquids in particular, the researches of Professor Kopp have shown that their atomic volumes are comparable only at temperatures for which the tensions of the vapours are equal; for example, at the boiling points of the liquids. If the atomic weights of liquids are compared with their densities at equal temperatures, no regular relations can be perceived; but when the same comparison is made at the boiling temperatures of the respective liquids, several remarkable laws become apparent. The density of a liquid at its boiling point cannot be ascertained by direct experiment; but when the density at any one point, say at 15·5° C. (60° F.), has been ascertained, and the rate of expansion is also known, the density at the boiling point may be calculated. Abundant data for these calculations are supplied by the labours of Kopp and Pierre (p. 644).

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* H. Kopp, Ann. Ch. Pharm. xcvi. 2, 330.

The following table contains Kopp's determinations of the atomic volumes of a considerable number of liquids containing carbon, hydrogen, and oxygen at their boiling points. The atomic weights are those of the hydrogen-scale. The *calculated* atomic volumes in the fourth column are determined by a method to be presently described; the *observed* atomic volumes in the fifth column are the quotients of the atomic weights, on the hydrogen-scale, divided by the specific gravities referred to water as unity.

TABLE A.

Atomic Volumes of Liquids containing Carbon, Hydrogen, and Oxygen.

	Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
				Calculated.	Observed.
Type HH.	Benzol	$Ꞓ_6H_6$	78	99·0	96·0... 99·7 at 80°
	Cymol	$Ꞓ_5H_{14}$	134	187·0	183·5...185·2 " 175
	Naphthalin	$Ꞓ_{10}H_8$	128	154·0	149·2. .... " 218
	Aldehyde	$Ꞓ_2H_4Ɵ_2$	44	56·2	56·0... 56·9 " 21
	Valeraldehyde	$Ꞓ_5H_{10}Ɵ_2$	86	122·2	117·3...120·3 " 101
	Bitter almond oil	$Ꞓ_7H_6Ɵ$	106	122·2	118·4......... " 179
	Cuminol	$Ꞓ_{10}H_6Ɵ$	148	188·2	189·2......... " 236
	Butyl	$Ꞓ_8H_{16}$	114	187·0	184·5...186·8 " 108
	Acetone	$Ꞓ_3H_6Ɵ$	58	78·2	77·3... 77·6 " 56
Type HH.Ɵ.	Water	$H_2Ɵ$	18	18·8	18·8......... " 100
	Wood-spirit	$ꞒH_4Ɵ$	32	40·8	41·9... 42·2 " 59
	Alcohol	$Ꞓ_2H_6Ɵ$	46	62·8	61·8... 62·5 " 78
	Amylic alcohol	$Ꞓ_5H_{12}Ɵ$	88	128·8	123·6...124·4 " 135
	Phenylic alcohol	$Ꞓ_6H_6Ɵ$	94	106·8	103·6...104·0 " 194
	Benzoic alcohol	$Ꞓ_7H_8Ɵ$	108	128·8	123·7........ " 213
	Formic acid	$ꞒH_2Ɵ_2$	46	42·0	40·9... 41·8 " 99
	Acetic acid	$Ꞓ_2H_4Ɵ_2$	60	64·0	63·5... 63·8 " 118
	Propionic acid	$Ꞓ_3H_6Ɵ_2$	74	86·0	85·4......... " 137
	Butyric acid	$Ꞓ_4H_8Ɵ_2$	88	108·0	106·4...107·8 " 156
	Valerianic acid	$Ꞓ_5H_{10}Ɵ_2$	102	130·0	130·2...131·2 " 175
	Benzoic acid	$Ꞓ_7H_6Ɵ_2$	122	130·0	126·9......... " 253
	Vinic ether	$Ꞓ_4H_{10}Ɵ$	74	106·8	105·6...106·4 " 34
	Acetic acid (anhydrous)	$Ꞓ_4H_6Ɵ_3$	102	109·2	109·9...110·1 " 138
	Formiate of methyl	$Ꞓ_2H_4Ɵ_2$	60	64·0	63·4......... " 36
	Acetate of methyl	$Ꞓ_3H_6Ɵ_2$	74	86·0	83·7... 85·8 " 55
	Formiate of ethyl	$Ꞓ_3H_6Ɵ_2$	74	86·0	84·9... 85·7 " 55
	Acetate of ethyl	$Ꞓ_4H_8Ɵ_2$	88	108·0	107·4...107·8 " 74
	Butyrate of methyl	$Ꞓ_5H_{10}Ɵ_2$	102	130·0	125·7...127·3 " 93
	Propionate of ethyl	$Ꞓ_5H_{10}Ɵ_2$	102	130·0	125·8......... " 93
	Valerate of methyl	$Ꞓ_6H_{12}Ɵ_2$	116	152·0	148·7...149·6 " 112
	Butyrate of ethyl	$Ꞓ_6H_{12}Ɵ_2$	116	152·0	149·1...149·4 " 112
	Acetate of butyl	$Ꞓ_6H_{12}Ɵ_2$	116	152·0	149·3......... " 112
	Formiate of amyl	$Ꞓ_6H_{12}Ɵ_2$	116	152·0	149·4...150·2 " 112
	Valerate of ethyl	$Ꞓ_7H_{14}Ɵ_2$	130	174·0	173·5...173·6 " 131
	Acetate of amyl	$Ꞓ_7H_{14}Ɵ_2$	130	174·0	173·3...175·5 " 131
	Valerate of amyl	$Ꞓ_{10}H_{20}Ɵ_2$	172	240·0	244·1......... " 188
	Benzoate of methyl	$Ꞓ_8H_8Ɵ_2$	136	152·0	148·5...150·3 " 190
	Benzoate of ethyl	$Ꞓ_9H_{10}Ɵ_2$	150	174·0	172·4...174·8 " 209
	Benzoate of amyl	$Ꞓ_{12}H_{16}Ɵ_2$	192	240·0	247·7......... " 266
	Cinnamate of ethyl	$Ꞓ_{11}H_{12}Ɵ_2$	176	207·0	211·3......... " 260
Type 2(HH.Ɵ).	Acid salicylate of methyl	$Ꞓ_8H_8Ɵ_3$	152	159·8	156·2...157·0 " 223
	Carbonate of ethyl	$Ꞓ_5H_{10}Ɵ_3$	118	137·8	138·8...139·4 " 126
	Oxalate of methyl	$Ꞓ_4H_8Ɵ_4$	118	117·0	116·3......... " 162
	Oxalate of ethyl	$Ꞓ_6H_{10}Ɵ_4$	146	161·0	166·8...167·1 " 186
	Succinate of ethyl	$Ꞓ_8H_{14}Ɵ_4$	174	205·0	209·0......... " 217

A comparison of the numbers in this table leads to the following remarkable results: —

1. *Differences of atomic volume are in numerous instances proportional to the differences between the corresponding chemical formulæ.* — Thus liquids, whose formulæ differ by $n\,.\,ȻH_2$, differ in atomic volume by $n\,.\,22$; for example, the atomic volumes of formiate of methyl, $Ȼ_2H_4\Theta_2$, and butyrate of ethyl, $Ȼ_6H_2\Theta_2$, differ by nearly 4 × 22. Acetate of ethyl, $Ȼ_4H_8\Theta_2$, and butyrate of methyl, $Ȼ_5H_{10}\Theta_2$, whose formulæ differ by $ȻH_2$, differ in atomic volume by nearly 22. The same law holds good with respect to liquids containing sulphur, chlorine, iodine, bromine, and nitrogen (see Tables B, C, D). Again: by comparing the atomic volumes of analogous chlorine and bromine compounds, it is found that the substitution of 1, 2, or 3 atoms of bromine for an equivalent quantity of chlorine, increases the atomic volume of a compound by once, twice, or three times 5. This will be seen by comparing the atomic volumes of PBr_3 and PCl_3; $Ȼ_2H_5Br$ and $Ȼ_2H_5Cl$, &c. (Table C.)

2. *Isomeric liquids belonging to the same chemical type have equal atomic volumes.*—The atomic volume of acetic acid, $\left.\begin{matrix}Ȼ_2H_3\Theta\\H\end{matrix}\right\}\Theta$, is between 63·5 and 63·8; that of formiate of methyl, $\left.\begin{matrix}ȻH\Theta\\ȻH_3\end{matrix}\right\}\Theta$, is 63·4; the atomic volume of butyric acid, $\left.\begin{matrix}Ȼ_4H_7\Theta\\H\end{matrix}\right\}\Theta$, is between 106·4 and 107·8; that of acetate of ethyl, $\left.\begin{matrix}Ȼ_2H_3O\\Ȼ_2H_5\end{matrix}\right\}\Theta$, is between 107·4 and 107·8.

3. *In liquids of the same chemical type, the replacement of hydrogen by an equivalent quantity of oxygen* (that is to say, of 1 pt. of hydrogen by 8 pts. of oxygen) *makes but a slight alteration in the atomic volume.* — This may be seen by comparing the atomic volumes of alcohol, $C_2H_6\Theta$, and acetic acid, $C_2H_4\Theta_2$; of ether, $C_4H_{10}\Theta$, acetate of ethyl, $C_4H_8\Theta_2$, and anhydrous acetic acid, $C_4H_6\Theta_3$; of cymol, $C_{10}H_{14}$, and cuminol, $C_{10}H_{12}\Theta$. The alteration caused by the substitution of Θ for H_6 is always an increase.

4. *In liquids of the same chemical type, the replacement of* 2 *at.* H *by* 1 *at.* Ȼ (1 pt. by weight of hydrogen by 6 parts of carbon) *makes no alteration in the atomic volume.* — Such, for example, is the case with benzoate of ethyl, $Ȼ_9H_{10}\Theta_2$, and valerate of ethyl, $Ȼ_7H_{14}\Theta_2$, and with the corresponding benzoates and valerates in general; also with bitter almond oil, $Ȼ_7H_6\Theta$, and valeraldehyde, $Ȼ_5H_{10}\Theta$.

In liquids belonging to different types, the same relations are not found to hold good. Moreover, the types within which these relations are observed, are precisely those of Gerhardt's classification (p. 696). Further, when liquid compounds are represented by rational formulæ founded on these types, their atomic volumes may be calculated from certain fundamental values of the atomic volumes of the elements, on the supposition that the atomic volume of a liquid compound is equal to the sum of the atomic volumes of its constituent elements.

Since the addition of $ȻH_2$ to a compound increases the atomic volume by 22, this number may be taken to represent the atomic volume of $ȻH_2$; moreover, since Ȼ (or C_2) may take the place of H_2 in combination, without altering the atomic volume of the compound, it follows that the atomic volume of Ȼ must be equal to that of H_2; and therefore the atomic volume of $Ȼ = \frac{22}{2} = 11$, and that of H_2 also equal to 11, or that of $H = 5{\cdot}5$. Further, as the substitution of Θ for H_2 produces a slight increase in the atomic volume of a compound, the atomic volume of Θ must be rather greater than 11; and it is found that, by assuming the atomic volume of Θ, when it takes the place of H_2 (that is to say, in a radical, as when acetyl, $Ȼ_2H_3\Theta$, is formed from ethyl, $Ȼ_2H_5$), to be equal to 12·2, results are obtained agreeing very nearly with those of observation. But when oxygen occupies the position which it has in water, $\begin{matrix}H\\H\end{matrix}\Theta$, its atomic volume is smaller. The specific gravity of water at the boiling point is 0·9579; hence its atomic volume at that temperature is $\frac{18}{0{\cdot}9579} = 18.8$; now the 2 atoms of hydrogen occupy a space equal to 11; hence the volume of the oxygen is 7·8. The same value of the atomic volume substituted for Ɵ in the formulæ of the several compounds belonging to the water-type, in which it occupies a similar place, that is to say, outside the radical, gives results agreeing nearly with observation. That a given quantity of a substance should occupy different spaces, under different circumstances, is a fact easily explained, when it is remembered that the particles of a body cannot be supposed to be in absolute contact, but are separated by certain spaces, which increase or diminish according to the temperature of the body, and according as it is in the solid, liquid, or gaseous state.

From these values of the atomic volumes of the elements carbon, hydrogen, and oxygen; viz. —

Atomic volume of Ꞓ .... = 11
“ “ H .... = 5·5
“ “ Ɵ (within the radical) .... = 12·2
“ “ Ɵ (without the radical) .... = 7·8;

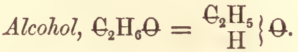
the calculated volumes of the atomic volumes of liquids, in the fourth column of Table A, are deduced. The method of calculation may be understood from the following examples:

Benzol, $\text{Ꞓ}_6\text{H}_6 = \text{Ꞓ}_6\text{H}_5 . \text{H}$.

Atomic volume of Ꞓ_6 .... = 66
“ “ H_6 .... = 33
“ “ benzol .... = 99

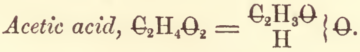
Aldehyde, $\text{Ꞓ}_2\text{H}_4\text{Ɵ} = \text{Ꞓ}_2\text{H}_3\text{Ɵ} . \text{H}$.

Atomic volume of Ꞓ_2 .... = 22
“ “ H_4 .... = 22
“ “ Ɵ (within the radical) .... = 12·2
“ “ aldehyde .... = 56·2



Alcohol, $\text{Ꞓ}_2\text{H}_6\text{Ɵ} = \left.\begin{matrix}\text{Ꞓ}_2\text{H}_5\\ \text{H}\end{matrix}\right\}\text{Ɵ}$.

Atomic volume of Ꞓ_2 .... = 22
“ “ H_6 .... = 33
“ “ Ɵ (without the radical) .... = 7·8
“ “ alcohol .... = 62·8



Acetic acid, $\text{Ꞓ}_2\text{H}_4\text{Ɵ}_2 = \left.\begin{matrix}\text{Ꞓ}_2\text{H}_3\text{Ɵ}\\ \text{H}\end{matrix}\right\}\text{Ɵ}$.

Atomic volume of Ꞓ_2 .... = 22
“ “ H_4 .... = 22
“ “ Ɵ (within the radical) .... = 12·2
“ “ Ɵ (without the radical) .... = 7·8
“ “ acetic acid .... = 64·0

Anhydrous acetic acid, $Ꞓ_4H_6Ɵ_3 = \left.\begin{matrix}Ꞓ_2H_3Ɵ\\ Ꞓ_2H_3Ɵ\end{matrix}\right\}Ɵ.$

Atomic volume of $Ꞓ_4$ .... = 44
" " H_6 .... = 33
" " $Ɵ_2$ (within the radical) .... = 24·4
" " $Ɵ$ (without the radical) .... = 7·8

" " anhydrous acetic acid .... = 109·2

Oxalate of methyl, $Ꞓ_4H_6Ɵ_4 = \left.\begin{matrix}Ꞓ_2Ɵ_2\\ (ꞒH_3)_2\end{matrix}\right\}Ɵ_2.$

Atomic volume of $Ꞓ_4$ .... = 44
" " H_6 .... = 33
" " $Ɵ_2$ (within the radical) .... = 24·4
" " $Ɵ_2$ (without the radical) .... = 15·6

" " oxalate of methyl .... = 117·0

Liquids containing Sulphur. — Sulphur enters into combination in various ways; sometimes taking the place of oxygen in the type $HH.Ɵ$ (as in mercaptan); sometimes taking the place of carbon within a radical (as in anhydrous sulphurous acid) $ꞨƟ.Ɵ$, compared with anhydrous carbonic acid, $ꞒO.Ɵ$; sometimes replacing oxygen within a radical (as in sulphide of carbon), $ꞒꞨ.Ꞩ$, compared with anhydrous carbonic acid. In the first and second cases, the atomic volume of sulphur-compounds may be calculated by attributing to sulphur ($Ꞩ = 32$), the atomic volume 22·6, those of the other elements remaining as above; in the third case, the atomic volume of sulphur appears to be greater; viz., 28·6.

Examples. — *Mercaptan*, $Ꞓ_2H_6Ꞩ = \left.\begin{matrix}Ꞓ_2H_5\\ H\end{matrix}\right\}Ꞩ.$

Atomic volume of $Ꞓ_2$ .... = 22
" " H_6 .... = 33
" " $Ꞩ$ .... = 22·6

" " mercaptan .... = 77·6

Sulphide of carbon, $ꞒꞨ_2 = ꞒꞨ·S.$

Atomic volume of $Ꞓ$ .... = 11
" " $Ꞩ$ (within the radical) .... = 28·6
" " $Ꞩ$ (without the radical) .... = 22·6

" " sulphide of carbon .... = 62·2

TABLE B.

Atomic Volumes of Liquid Sulphur-compounds.

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Mercaptan	$Ꞓ_2H_6Ꞩ$	62	77·6	76·0... 76·1 at 36° C.
Amylic mercaptan	$Ꞓ_5H_{12}Ꞩ$	104	143·6	140·1...140·5 " 120
Sulphide of methyl	$Ꞓ_2H_6Ꞩ$	62	77·6	75·7......... " 41
Sulphide of ethyl	$Ꞓ_4H_{10}Ꞩ$	90	121·6	120·5...121·5 " 91
Bisulphide of methyl	$Ꞓ_2H_6Ꞩ_2$	94	100·2	100·6...100·7 " 114
Sulphurous acid	$ꞨƟ_2$	64	42·6	43·9......... " —8
Sulphite of ethyl	$Ꞓ_4H_{10}ꞨƟ_3$	138	149·4	148·8...149·5 " 160
Bisulphide of carbon	$ꞒꞨ_2$	76	62·2	62·2... 62·4 " 47

Chlorides, Bromides, and Iodides. — In liquid compounds of this class, the atomic volume of Cl is supposed to be 22·8, that of Br = 27·8, and that of I = 37·5, those of the other elements remaining as above.

Table C.

Atomic Volumes of Liquid Chlorides, Bromides, and Iodides.

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Bichlorinated ethylene	$Ꞓ_2H_2Cl_2$	97	78·6	79·9.......... at 37° C.
Chloride of carbon	$Ꞓ_2Cl_4$	166	113·2	115·4.......... " 123
Chloride of ethylene	$Ꞓ_2H_4Cl_2$	99	89·6	85·8... 86·4 " 85
———, monochlorinated	$Ꞓ_2H_3Cl_3$	133·5	106·9	105·4...107·2 " 115
———, bichlorinated	$Ꞓ_2H_2Cl_4$	168	124·2	120·7...121·4 " 137
———, terchlorinated	$Ꞓ_2HCl_5$	202·5	141·5	143 .... " 154
Chloride of butylene	$Ꞓ_4H_8Cl_2$	127	133·6	129·5...133·7 " 123
Monochlorinated chloride of methyl	$ꞒH_2Cl_2$	85	67·6	64·5.......... " 30·5
Chloroform	$ꞒHCl_3$	119·5	84·9	84·8... 85·7 " 62
Chloride of carbon	$ꞒCl_4$	154	102.2	104·3...107·0 " 78
Chloride of ethyl	$Ꞓ_2H_5Cl$	64·5	72·3	71·2... 74·5 " 11
———. monochlorinated	$Ꞓ_2H_4Cl_2$	99	89·6	86·9... 89·9 " 64
———, bichlorinated	$Ꞓ_2H_3Cl_3$	133·5	106·9	105·6...109·7 " 75
Chloride of amyl	$Ꞓ_5H_{11}Cl$	106·5	138·3	135·4...137·0 " 102
Chloral	$Ꞓ_2HCl_3Ɵ$	147·5	108·1	108·4...108·9 " 96
Chloride of acetyl	$Ꞓ_2H_3ƟCl$	78·5	73·5	74·4... 75·2 " 55
Chloride of benzoyl	$Ꞓ_7H_5ƟCl$	140·5	139·5	134·2...137·8 " 198
Bromine	Br_2	160	55·6	54 ... 57·4 " 63
Bromide of methyl	$ꞒH_3Br$	95	55·3	58·2.......... " 13
Bromide of ethyl	$Ꞓ_2H_5Br$	109	77·3	78·4.......... " 41
Bromide of amyl	$Ꞓ_5H_{11}Br$	151	143·3	149·2.......... " 119
Bromide of ethylene	$Ꞓ_2H_4Br_2$	188	99·6	97·5... 99·9 " 130
Iodide of methyl	$ꞒH_3I$	142·1	65·0	65·4... 68·3 " 43
Iodide of ethyl	$Ꞓ_2H_5I$	156·1	87·0	85·9... 86·4 " 71
Iodide of amyl	$Ꞓ_5H_{11}I$	198·1	153·0	152·5...155·8 " 147
Chloride of sulphur	$ꞨCl$	67·5	......	45·7.......... " 140
Chloride of phosphorus	PCl_3	137·5	......	93·9.......... " 78
Bromide of phosphorus	PBr_3	271	......	108·6.......... " 175
Chloride of silicon	$SiCl_3$	127·8	......	91·6.......... " 59
Bromide of silicon	$SiBr_3$	261·3	......	108·2.......... " 153
Chloride of arsenic	$AsCl_3$	181·5	......	94·8.......... " 133
Chloride of antimony	$SbCl_3$	235·5	......	100·7.......... " 223
Bromide of antimony	$SbBr_3$	369	......	116·8.......... " 275
Chloride of tin	$SnCl_2$	129	......	65·7.......... " 115
Chloride of titanium	$TiCl_2$	96	......	63·0.......... " 136

The compounds PCl_3, $SiCl_3$, and $AsCl_3$, have nearly equal atomic volumes, whence it may be inferred that phosphorus, silicon, and arsenic, in their liquid compounds, have equal atomic volumes. The same conclusion may be drawn regarding tin and titaninum, since the atomic volumes of $SnCl_2$ and $TiCl_2$ are equal.

Nitrogen-compounds. — In compounds belonging to the ammonia type, the atomic volume of nitrogen is 2·3. This result is deduced from the observed atomic volume of aniline, $Ꞓ_6H_7N$, which is 106·8. Now the atomic volume of $6\,Ꞓ + 7\,H = 6 . 11 + 7 . 5{\cdot}5 = 104{\cdot}5$, which number, deducted from 106·8 leaves 2·3 for the atomic volume of nitrogen.

The atomic volume of cyanogen deduced from the observed at. vol. of cyanide of phenyl, $CN . C_6H_5$, or C_7H_5N, is nearly 28. Thus —

$$\begin{array}{lll} \text{Atomic volume of } C_7H_5N & = & 121{\cdot}6 \\ \text{“} \quad \text{“} \quad C_6H_5 & = & 93{\cdot}5 \\ \hline \text{“} \quad \text{“} \quad CN & = & 28{\cdot}1 \end{array}$$

A similar calculation, founded on the observed atomic volume of cyanide of methyl, C_2H_3N, gives, for the at. vol. of cyanogen, the number 26·8. The atomic volume of liquid cyanogen determined directly at 37° or 39° C. above its boiling point, is between 28·9 and 30·0. As a mean of these values, the atomic volume of cyanogen may be assumed to be 28; and with this value the atomic volumes of the liquid cyanides are calculated. Thus, for

$$\text{Oil of mustard (sulpho-cyanide of allyl), } C_4H_5NS = \left.\begin{matrix} CN \\ C_3H_5 \end{matrix}\right\} S.$$

$$\begin{array}{lll} \text{Atomic volume of } C_3H_5 \ldots\ldots\ldots\ldots\ldots\ldots & = & 60{\cdot}5 \\ \text{“} \quad \text{“} \quad CN \ldots\ldots\ldots\ldots\ldots\ldots\ldots & = & 28{\cdot}0 \\ \text{“} \quad \text{“} \quad S \text{ (without the radical)} \ldots\ldots & = & 22{\cdot}6 \\ \hline \text{“} \quad \text{“} \quad \text{oil of mustard} \ldots\ldots\ldots\ldots & = & 111{\cdot}1 \end{array}$$

The atomic volumes of compounds containing the radical NO_2, are calculated on the hypothesis that the at. vol. of that radical is 33, which agrees nearly with the observed atomic volume of liquid peroxide of nitrogen. Thus:—the at. vol. of nitrate of amyl, $C_5H_{11}NO_2$ = at vol. of C_5H_{11} + at. vol. of NO_2 = 115·5 + 33 = 148·5.

TABLE D.

Atomic Volumes of Liquids containing Nitrogen.

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Ammonia	H_3N	17	18·8	22·4 .. 23·3 at 10° . 16°*
Ethylamine	C_2H_7N	45	62·8	65·3 .... at 18·7
Butylamine	$C_4H_{11}N$	73	106·8	
Amylamine	$C_5H_{13}N$	87	128·8	125·0 .... “ 94
Caprylamine	$C_8H_{19}N$	129	194·8	190·0 .... “ 170
Aniline	C_6H_7N	93	106·8	106·4 . 106·8...... “ 184
Toluidine	C_7H_9N	107	128·8	
Ethaniline	$C_8H_{11}N$	121	150·8	150·6 .... “ 204
Biethaniline	$C_{10}H_{15}N$	149	194·8	190·5 .... “ 213·5
Cyanogen	CN	26	28·0	28·9 . 30·0...... “ 16†
Hydrocyanic acid	CHN	27	33·5	39·1 .... “ 27
Cyanide of methyl	C_2H_3N	41	55·5	54·3 .... “ 74
Cyanide of ethyl	C_3H_5N	55	77·5	77·2 .... “ 88
Cyanide of butyl	C_5H_9N	83	121·5	
Cyanide of phenyl	C_7H_5N	103	121·5	121·6 . 121·9...... “ 191
Sulphycyanide of methyl	C_2H_3NS	73	78·1	75·2 . 78·2...... “ 133
Sulphocyanide of ethyl	C_3H_5NS	87	100·1	99·1 .... “ 146
Oil of mustard	C_4H_5NS	99	111·1	113·1 · 114·2...... “ 148
Cyanate of ethyl	C_3H_5NO	71	85·3	84·3 · 84·8...... “ 60
Peroxide of nitrogen	NO_3	30	33·0	31·7 · 32·4...... “ 40‡
Nitrate of methyl	CH_3NO_3	77	68·3	69·4 .... “ 66
Nitrate of ethyl	$C_2H_5NO_3$	101	90·3	90·0 . 90·1...... “ 86
Nitrobenzol	$C_6H_5NO_2$	123	126·5	122·6 . 124·9...... “ 218
Nitrite of methyl	CH_3NO_2	61	60·5	61·6 .... “ 14§
Nitrite of ethyl	$C_2H_5NO_2$	75	82·5	79·2 . 84·6...... “ 18
Nitrite of amyl	$C_5H_{11}NO_2$	117	148·5	148·4 .... “ 95

* Between 44° and 50° above the boiling point.

† Between 37° and 39° above the boiling point.

‡ About 35° above the boiling point.

§ 27° above the boiling point.

From the preceding observations and calculations, it appears that the atomic volume of a compound depends, not merely on its empirical, but likewise on its rational formula; in other words, not merely on the number of atoms of its elements, but further on the manner in which those atoms are arranged. Now it has been shown (p. 693) that a compound may have more than one rational formula, according to the manner in which it decomposes; and hence it might appear that the calculation of atomic volumes must be attended with considerable uncertainty, inasmuch as the atomic volumes of certain elements, as oxygen and sulphur, vary according to the manner in which they enter into the compound. Aldehyde, for example, may be represented either as $\left.\begin{matrix}Ꞓ_2H_3\\H\end{matrix}\right\}Ɵ$, or as $\left.\begin{matrix}Ꞓ_2H_3\\H\end{matrix}\right\}Ɵ$; and, as the atomic volume of oxygen is 12·2 or 7·8, according as it is within or without the radical, the atomic volume of aldehyde will be 56·2 if deduced from the type HH, and 51·8 if deduced from the type HH.Ɵ. But the atomic weight of aldehyde, and its specific gravity at a given temperature are invariable; it cannot, therefore, have two different atomic volumes. It must beremembered, however, that, in speaking of a compound as having several rational formulæ, we consider it rather in a dynamical than in a statical point of view; as under the influence of disturbing forces, and on the point of undergoing chemical change. But if, on the other hand, we regard a compound in its fixed statical condition, as a body possessing definite physical properties, a certain specific gravity, a certain boiling point, rate of expansion, refractive power, &c., we can scarcely avoid attributing to it a fixed molecular arrangement, or, at all events, supposing that the disposition of its atoms is confined within those limits which constitute chemical types. It is found, indeed, that isomeric liquids exhibit equal atomic volumes only when they belong to the same chemical type. If this view be correct, the relation between the atomic volumes of elements and compounds, may often render valuable service in determining the rational formula which belongs to a compound in the state of rest. Thus, of the two atomic volumes just calculated for aldehyde, the number 56·2, deduced from the formula, $Ꞓ_2H_3Ɵ.H$, agrees with the observed atomic volume of aldehyde, which is between 56·0 and 56·9, better than 51·8, the number deduced from $\left.\begin{matrix}Ꞓ_2H_3\\H\end{matrix}\right\}Ɵ$. This result leads to the conclusion that the aldehydes belong to the hydrogen-type (p. 718), rather than to the water-type.

There are many groups of liquid compounds, irrespective of isomerism or similarity of type, the members of which have equal or nearly equal atomic volumes. The following table exhibits the calculated atomic volumes of several of these groups :—

Atomic Volume of Liquids.

Water	$H_2Ɵ$	18·8	Ether	$Ꞓ_4H_{10}Ɵ$	106·8
Ammonia	NH_3	18·8	Butylic alcohol	$Ꞓ_4H_{10}Ɵ$	106·8
			Phenylic alcohol	$Ꞓ_6H_6Ɵ$	106·8
Bromine	Br_2	55·6	Butylamine	$Ꞓ_4H_{11}N$	106·8
Cyanogen	$(ꞒN)_2$	56·0	Aniline	$Ꞓ_6H_7N$	106·8
Aldehyde	$Ꞓ_2H_4Ɵ$	56·2	Butyric acid	$Ꞓ_4H_8Ɵ_2$	108·0
Cyanide of methyl	$Ꞓ_2H_3N$	55·5	Acetate of ethyl	$Ꞓ_4H_8Ɵ_2$	108·0
Bromide of methyl	$Ꞓ_2H_3Br$	55·3	Anhydrous acetic acid	$Ꞓ_4H_6Ɵ_3$	109·2
			Chloral	$Ꞓ_2HClƟ$	108·1
Alcohol	$Ꞓ_2H_6Ɵ$	62·8	Bichlorinated chloride of ethyl	$Ꞓ_2H_3Cl_3$	106·9
Acetic acid	$Ꞓ_2H_4Ɵ_2$	64·0			
Formiate of methyl	$Ꞓ_2H_4Ɵ_2$	64·0	Monochlorinated chloride of ethylene	$Ꞓ_2H_3Cl_3$	106·9
Cyanate of methyl	$Ꞓ_2H_3NƟ_2$	63·3			
Ethylamine	$Ꞓ_2H_7N$	62·8	Bromide of phosphorus	PBr_3	108·6
Sulphide of carbon	$ꞒꞨ_2$	62·3			
Iodide of methyl	$ꞒH_3I$	65·0	Valeraldehyde	$Ꞓ_5H_{10}Ɵ$	122·2
			Cyanide of butyl	$Ꞓ_5H_9N$	121·5
Acetone	$Ꞓ_3H_6Ɵ$	78·2	Bitter almond oil	$Ꞓ_7H_6Ɵ$	122·2
Cyanide of ethyl	$Ꞓ_3H_5N$	77·5	Cyanide of phenyl	$Ꞓ_7H_5N$	121·5
Sulphocyanide of methyl	$Ꞓ_2H_3NꞨ$	78·1	Sulphide of ethyl	$Ꞓ_4H_{10}Ꞩ$	121·6
Sulphide of methyl	$Ꞓ_2H_6Ꞩ$	77·6			

These groups exhibit an approach to the uniformity of atomic volume which is observed in the gaseous state.

Berthelot has adduced a number of examples, showing that when a liquid compound is formed by the union of two other liquids, whose specific volumes are denoted by A and B, with elimination of x atoms of water, the specific volume of the compound is nearly $= A + B - xC$ (the atomic volume of water being denoted by C). Berthelot's observations, however, were made at medium temperatures, not at the boiling points of the liquids.

Atomic Volume of Solids.—The principal results obtained by Kopp, with reference to the atomic volume of solid bodies, are given in pp. 172–176.* The difficulty of reducing the results to general laws is similar to that which has been noticed in the case of liquids, but exists to a still greater extent, inasmuch as our knowledge of the expansion of solids by heat is much more limited than that of liquids. It is probable that the atomic volumes of solids should be compared at their melting points; since it is only at those temperatures that the effects of heat upon different solids can be said to be equal. Now the specific gravities of most solids are determined only at medium temperatures, from which the melting points of different solids are separated by intervals of very different magnitude; moreover, there are but few solids whose rate of expansion at different temperatures has been ascertained with sufficient accuracy to render it possible to calculate the specific gravities at the melting points. A further complication arises from the different densities which the same solid often exhibits, according as it is amorphous or crystalline, or according to the particular form in which it crystallizes.

RELATIONS BETWEEN CHEMICAL COMPOSITION AND BOILING POINT.†

In compounds of similar constitution, and especially among the members of homologous series (p. 699), difference of boiling point is frequently proportional to difference of composition.

1. In the alcohols, $Ꞓ_nH_{2n+2}Ɵ$, the fatty acids, $Ꞓ_nH_{2n}Ɵ_2$, and the compound ethers (p. 705) isomeric with the fatty acids, a difference of $ꞒH_2$ in the formula corresponds to a difference of 19° C. in the boiling point.

2. The boiling point of a fatty acid, $Ꞓ_nH_{2n}Ɵ_2$, is higher by 40° C. than that of the corresponding alcohol, $Ꞓ_nH_{2n+2}Ɵ$.

3. The boiling point of a compound ether, $Ꞓ_nH_{2n}Ɵ_2$, is lower by 82° C. than that of the isomeric acid.

Starting from the observed boiling point of common alcohol, 78° C., and calculating by these rules the boiling points of the other alcohols and of the fatty acids and ethers, we obtain the numbers in the third column of the following table, which do not differ from the observed boiling points in the fourth column, more than these latter, as determined by different observers, differ from one another.

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* The numbers there given refer to the oxygen-scale of atomic weights. (O = 100.)

† H. Kopp. Ann. Ch. Pharm. xcvi. 2, 330.

Substance.	Formula.	Boiling point. Calculated.	Boiling point. Observed.	Observers.
Alcohols.				
Methylic alcohol	$\text{Ꞓ}H_4\Theta$	59°	60° .... at 744 mm.	Kane.
			61 .... “ 755 “	Delffs.
			64·9 .... “ 754 “	H. Kopp.
			65 .... “ 752 “	H. Kopp.
Propylic alcohol	$\text{Ꞓ}_3H_8\Theta$	97	96 .... “ ? “	Chancel.
Butylic alcohol	$\text{Ꞓ}_4H_{10}\Theta$	116	109 .... “ ? “	Wurtz.
Amylic alcohol	$\text{Ꞓ}_5H_{12}\Theta$	135	130·4 .... “ 742 “	H. Kopp.
			132 .... “ 760 “	Cahours.
			132 .... “ 766 “	Delffs.
Cetylic alcohol	$\text{Ꞓ}_{16}H_{34}\Theta$	344	360 .... “ ? “	Favre and Silbermann.
Acids.				
Formic acid	$\text{Ꞓ}H_2\Theta_2$	99	98·5 .... “ 753 “	Liebig.
			105·4 .... “ 764 “	H. Kopp.
Acetic acid	$\text{Ꞓ}_2H_4\Theta_2$	118	116·9 .... “ 750 “	H. Kopp.
			116 .... “ 754 “	Delffs.
Propionic acid	$\text{Ꞓ}_3H_6\Theta_2$	137	141·6 .... “ 754·6 “	H. Kopp.
			141 .... “ ? “	Limpricht & v. Uslar.
Butyric acid	$\text{Ꞓ}_4H_8\Theta_2$	156	156 .... “ 733 “	H. Kopp.
			163 .... “ 751 “	I. Pierre.
Valerianic acid	$\text{Ꞓ}_5H_{10}\Theta_2$	175	174·5 .... “ 762 “	Delffs.
			175·8 .... “ 746·5 “	H. Kopp.
Caproic acid	$\text{Ꞓ}_6H_{12}\Theta_2$	194	198 .... “ ? “	Brazier and Gossleth.
Caprylic acid	$\text{Ꞓ}_8H_{16}\Theta_2$	232	236 .... “ ? “	Fehling.
Pelargonic acid	$\text{Ꞓ}_9H_{18}\Theta_2$	251	260 .... “ ? “	Cahours.
Compound Ethers.				
Formiate of methyl ...	$\text{Ꞓ}_2H_4\Theta_2$	36	32·7 .... “ 741 “	H. Kopp.
			22·9 .... “ 752 “	Andrews.
Acetate of methyl	$\text{Ꞓ}_3H_6\Theta_2$	55	55 .... “ 762 “	Andrews.
			57·7 .... “ 757 “	H. Kopp.
			59·5 .... “ 761 “	I. Pierre.
Formiate of ethyl	$\text{Ꞓ}_3H_6\Theta_2$	55	52·9 .... “ 752 “	I. Pierre.
			53 .... “ 736 “	Delffs.
			54·7 .... “ 754 “	H. Kopp.
Acetate of ethyl	$\text{Ꞓ}_4H_8\Theta_2$	74	73·7 .... “ 745 “	H. Kopp.
			74·1 .... “ 766 “	I. Pierre.
Butyrate of methyl ...	$\text{Ꞓ}_5H_{10}\Theta_2$	93	93 .... “ 744 “	Delffs.
			95·1 .... “ 742 “	H. Kopp.
			102·1 .... “ 744 “	I. Pierre.
Acetate of propyl	$\text{Ꞓ}_5H_{10}\Theta_2$	93	90 (about)	Berthelot.
Propionate of ethyl ...	$\text{Ꞓ}_5H_{10}\Theta_2$	93	95·8 ... 98 “	H. Kopp.
Valerate of methyl ...	$\text{Ꞓ}_6H_{12}\Theta_2$	112	114 . 115 “ 756 “	H. Kopp.
Butyrate of ethyl	$\text{Ꞓ}_6H_{12}\Theta_2$	112	114·6 .... “ 756 “	H. Kopp.
			119 .... “ 747 “	I. Pierre.
Formiate of amyl	$\text{Ꞓ}_6H_{12}\Theta_2$	112	114 .... “ 771 “	Delffs.
			116 (about)	H. Kopp.
Acetate of butyl	$\text{Ꞓ}_2H_{12}\Theta_2$	112	114	Wurtz.
Valerate of ethyl	$\text{Ꞓ}_7H_{14}\Theta_2$	131	131·3 .... “ 735 “	Delffs.
			133·2 .... “ 754 “	H. Kopp.
Acetate of amyl	$\text{Ꞓ}_7H_{14}\Theta_2$	131	133 .... “ 760 “	Delffs.
			133·3 .... “ 749 “	H. Kopp.
			137·6 .... “ 746 “	H. Kopp.
Valerate of amyl	$\text{Ꞓ}_{10}H_{20}\Theta_2$	188	187·8 . 188·3 “ 730 “	H. Kopp.

It appears from this table that isomeric compound ethers have equal boiling points; *e. g.*, formiate of ethyl and acetate of methyl boil at 55°; valerate of methyl, butyrate of ethyl, formiate of amyl, and acetate of butyl, boil at 112°.

It follows, also, from the preceding laws, that the boiling point of an acid, $C_nH_{2n}O_2$, is 63° higher than that of its methylic ether, 44° higher than that of its ethylic ether, and 13° lower than that of its amylic ether: thus, valerianic acid boils at 175°; valerate of methyl at 112°; valerate of ethyl at 131°; valerate of amyl at 188°. Common ether, $(C_2H_5)_2O$, is the ethyl-salt of alcohol, $\left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}O$, regarded as an acid; that is to say, it bears the same relation to alcohol that acetate of ethyl bears to acetic acid: hence its boiling point should be 78°—44° =34°. The actual observations of the boiling point of ether vary from 34° to 35·7°.

In the same series of homologous compounds, it is found that the addition of nC raises the boiling point by $n.\,29°$; and the addition of nH lowers the boiling point by $n.5°$ [consequently, the addition of nCH_2 raises it by $n.(29 - 2 \times 5) = n.19°$]. The same law is likewise observed in other series of compounds of similar character. Thus, benzoate of ethyl, $C_9H_{10}O_2$, boils at 209°, which is higher by 4×29, or 116, than the boiling point of the ethers, $C_5H_{10}O_2$,—butyrate of methyl for example. The boiling point of angelic acid, $C_5H_8O_2$, is higher by 29° than that of butyric acid, $C_4H_8O_2$; and 2×5, or 10°, higher than that of valerianic acid, $C_5H_{10}O_2$. The boiling point of phenylic alcohol, C_6H_6O, is higher by about 4×29, or 116°, than that of common alcohol, C_2H_6O; and about 8×5, or 40°, higher than that of caproic alcohol, $C_6H_{14}O$.

Constant relations of composition and boiling point are observed also in other series of homologous compounds; but the difference of boiling point corresponding with a difference of CH_2, is not always 19°. In the series of hydrocarbons:—benzol, C_6H_6 (B.P. 80°), toluol, C_7H_8, xylol, C_8H_{10}, cumol, C_9H_{12}, cymol, $C_{10}H_{14}$, the difference is 24°; in the homologous compounds:—bromide of ethylene, $C_2H_4Br_2$, bromide of propylene, $C_3H_6Br_2$, bromide of butylene, $C_4H_8Br_2$, it is 15°, their boiling points being 130°, 145°, and 160°, respectively. In the series of alcohol-radicals (in the free state), the difference is about 23°; in the anydrous acids, homologous with anhydrous acetic acid, it is about 13°.

These differences of boiling point would probably be the same in all series of homologous compounds, if the boiling points were determined at different pressures. It is not, indeed, to be expected that two substances should exhibit the same difference of boiling point under all pressures; for if B and B′ denote the boiling points of two liquids at the ordinary atmospheric pressure, b and b′, the boiling points of the same liquids at another pressure; and if we suppose that

$$B - B' = b - b',$$

it will follow that

$$B - b = B' - b';$$

that is to say, the boiling points of the two liquids would vary equally for equal differences of pressure, which is contrary to observation.

CHEMICAL AFFINITY.

Influence of mass on chemial action.—That the relative degrees of affinity of a body for a number of others to which it is simultaneously presented, are greatly modified by their relative masses, was first pointed out by Berthollet. The law laid down by that philosopher respecting the action of masses, is this:—*A body to which two different substances, capable of uniting with it chemically, are pre-*

sented in different proportions, divides itself between them in the ratio of the products of their masses, and the absolute strengths of their affinities for the first body. Thus, if we denote by A and B the masses of the two bodies which are present in excess, by α and β, the coefficients of their absolute affinities for the body C; and by a and b, the quantities of A and B, which actually combine with C, the law just stated will be expressed by the proportion: —

$$a : b = \alpha A : \beta B.$$

If this view be correct, any alteration, however small, in the relative quantities of A and B, must produce a corresponding alteration in the relative quantities of the two which unite with C. That this is not the case under all circumstances, is shown by the following experiments of Bunsen and of Debus.

Bunsen's experiments,* which were made in such a manner that all the phenomena of combination concerned in them took place simultaneously, lead to the following remarkable laws:—

1. When two or more bodies, BB' . . . are presented in excess to the body A, under circumstances favourable to their combination with it, the body A always selects of the bodies BB' . . . quantities which stand to one another in a simple atomic relation, so that for 1, 2, 3 . . . atoms of the one compound, there are always formed 1, 2, 3 . . . atoms of the other; and if in this manner there is formed an atom of the compound AB' in conjunction with an atom of AB, the mass of the body B may be increased relatively to that of B', up to a certain limit, without producing any alteration in the atomic proportion.

When carbonic oxide and hydrogen are exploded with a quantity of oxygen not sufficient to burn them completely, the oxygen divides itself between the two gases in such a manner that the quantities of carbonic acid and water produced stand to one another in a simple atomic proportion. The results of Bunsen's experiments are given in the following table, the numbers in which denote volumes: —

Composition of Gaseous Mixture.			Quantities of CO and H consumed by Detonation.		Ratio of CO : H.
72·57 CO	18·29 H	9·14 O	12·18 CO	6·10 H	2 : 1
59·93 “	26·71 “	13·36 “	13·06 “	13·66 “	1 : 1
36·70 “	42·17 “	21·13 “	10·79 “	31·47 “	1 : 3
40·12 “	47·15 “	12·73 “	4·97 “	20·49 “	1 : 4

The results were the same whether the explosion took place in the dark, in diffused daylight, or in sunshine; and were not affected by the pressure to which the gaseous mixture was subjected.

The proportions of hydrogen and carbonic acid consumed in these several experiments, correspond with the composition of five hydrates of carbonic acid, containing, respectively —

$$HO.2CO_2;\ HO.CO_2;\ 2HO.CO_2;\ 3HO.CO_2;\ 4HO{\cdot}CO_2;$$

but the results cannot be attributed to the actual formation of these hydrates, inasmuch as hydrates of acids containing several atoms of water are incapable of existing at high temperatures.

2. When a body, A, exerts a reducing action on a compound, BC, present in excess, so that A and B combine together, and C is set free; then, if C can, in its turn, exert a reducing action on the newly-formed compound, AB, the final result of the action is, that the reduced portion of BC is to the unreduced portion in a simple atomic proportion.

In this case, also, the mass of the one constituent may, without altering the

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* Ann. Ch. Pharm. lxxxv. 137.

existing atomic relation, be increased to a certain limit, above which that relation undergoes changes by definite steps, but always in the proportion of simple rational numbers.

When vapour of water is passed over red-hot charcoal, the carbon is oxidized and hydrogen is separated; but the process does not go on so far as the complete formation of carbonic acid, but stops at the point at which 1 vol. carbonic acid and 2 vol. carbonic oxide are formed to every 4 vol. of hydrogen.

In the imperfect combustion of cyanogen—the gaseous mixture being so far diluted that it will but just explode, in order that the temperature may not rise too high, and the result be consequently vitiated by the partial oxidation of the nitrogen—carbonic acid and carbonic oxide are formed, and nitrogen set free, likewise in simple atomic proportion. A mixture of 18·05 vol. cyanogen, 28·87 oxygen, and 53·08 nitrogen, gave, by detonation, 2 vol. carbonic oxide, and 4 vol. carbonic acid to 3 vol. nitrogen.

In the combustion of a mixture of carbonic acid, hydrogen, and oxygen, in which the carbonic acid is exposed at the same time to the reducing action of the hydrogen and the oxidizing action of the oxygen, the reduced portion of the carbonic acid is likewise found to bear to the unreduced portion a simple atomic relation. In the combustion of a mixture of 8·52 carbonic acid, 70·33 hydrogen, and 21·15 oxygen, the resulting carbonic oxide was to the reduced carbonic acid in the ratio of 3 : 2. After the combustion of a mixture of 4·41 vol. carbonic oxide, 2·96 carbonic acid, 68·37 hydrogen, and 24·<6 oxygen, the volume of the carbonic oxide converted into carbonic acid by oxidation, was to that of the residual carbonic oxide as 1 : 3.

That these remarkable laws had not been previously observed is attributed by Bunsen to the fact that they held good only when the phenomena of combination, which are regulated by them, take place simultaneously; for, even if a body *A*, were originally to select for combination from the bodies *B* and *C*, quantities bearing to one another a simple atomic relation, but the combination of *A* and *B* were to take place in a shorter time than that of *A* and *C*, it would follow of necessity, that during the whole of the process, the ratio of *B* to *C*, and therefore, also the atomic relations of the associated compounds, would change, so that the observed proportion would be no longer definite. The same result must follow if the bodies which are combining side by side are not homogeneously mixed in the beginning.

With regard to the bearing of these results on Berthollet's law, it might be objected that, in some of the experiments, as in the combustion of a mixture of carbonic oxide, hydrogen, and oxygen, one of the products, viz. the water, is removed from the sphere of action by condensation, and that the circumstances are therefore similar to the removal of an insoluble product by precipitation (p. 185). It is scarcely conceivable, however, that a reverse action would take place, even if the gaseous mixture were to remain at the temperature which exists during the combustion. Moreover, in the decomposition of vapour of water by red-hot charcoal, the whole of the products remain in the gaseous state.

Debus* has obtained results similar to those of Bunsen by precipitating mixtures of lime and baryta-water with aqueous carbonic acid, or mixtures of chloride of barium and chloride of calcium, with carbonate of soda. A small quantity of a very dilute solution of carbonate of soda, added to a liquid containing 5 pts. of chloride of barium to 1 pt. of chloride of calcium, threw down nearly pure carbonate of lime; but when the proportion of the chloride of barium in the mixture was 5·7 times as great as that of the chloride of calcium, 2·3 pts. of the former were decomposed to 1 pt. of the latter. Hence it appears that, in this reaction also, limits exist at which the ratio of the affinities undergoes a sudden change. In these experiments, however, the products are immediately removed from the

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* Ann. Ch. Pharm. lxxxv. 103; lxxxvi. 156; lxxxvii. 238.

sphere of action, and the results are therefore not comparable with those which are obtained when all the substances present remain mixed and free to act upon each other.

The latter condition is most completely fulfilled in the mutual actions of liquid compounds, such as solutions of salts, when all the possible products of their mutual actions are likewise soluble; as, for example, when nitrate of soda in solution is mixed with sulphate of copper. The question to be solved in such cases is this. Suppose two salts AB, CD, the elements of which can form only soluble products by their mutual interchange, to be mixed together in solution. Will these elements, according to their relative affinities, either remain in their original state of combination, as AB and CD, or pass completely into the new arrangement AD and CB?—or will each of the two acids divide itself between each of the two bases, producing the four compounds AB, AD, BC, BD?—and, if so, in what manner will the relative quantities of these four compounds be affected by the original quantities of the two salts? Do the amounts of AD and CB, produced by the reaction, increase progressively with the regular increase of AB, as required by Berthollet's theory? or do sudden transitions occur, like those observed in the experiments of Bunsen and Debus?

The solution of this question is attended with considerable difficulty. For when two salts in solution are mixed, and nothing separates out, it is by no means easy to ascertain what changes may have taken place in the liquid. The ordinary methods of ascertaining the composition of the mixture, such as concentration, or precipitation by re-agents, are inadmissible, because any such treatment immediately alters the mutual relation of the substances present. In some cases, however, the mixture of two salts is attended with a decided change of colour, without any separation of either of the constituents, and such alterations of colour may afford indications of the changes which take place in the arrangement of the molecules. This method has been employed by Dr. Gladstone,* who has carefully examined the changes of colour attending the mixture of a great variety of salts, and applied the results to the determination of the effect of mass in influencing chemical action.

Dr. Gladstone's principal experiments were made with the blood-red sulphocyanide of iron, which is formed on adding hydro-sulphocyanic acid or any soluble sulphocyanide to a solution of a ferric salt (p. 377). On mixing known quantities of different ferric salts with known quantities of different sulphocyanides, it was found that the iron was never completely converted into the red salt; that the amount of it so converted depended on the nature both of the acid combined with the ferric oxide, and of the base combined with the sulphocyanogen; and that it mattered not how the bases and acids had been combined previous to their mixture, so long as the same quantities were brought together in solution. The effect of mass was tried by mixing equivalent proportions of ferric salts and sulphocyanides, and then adding known amounts of one or the other compound. It was found that, in either case, the amount of the red salt was increased, and in a regular progression according to the quantity added. When sulphocyanide of potassium was mixed in various proportions with ferric nitrate, chloride, or sulphate, the rate of variation appeared to be the same, but with hydrosulphocyanic acid it was different. The deepest colour was produced when ferric nitrate was mixed with sulphocyanide of potassium; but even on mixing 1 eq. of the former with 3 eq. of the latter, only 0·194 eq. of the red sulphocyanide of iron was formed; and even when 375 eq. of sulphocyanide of potassium had been added, there was still a recognizable amount of ferric nitrate undecomposed. The results of a series of experiments with ferric nitrate and sulphocyanide of potassium are given in the following table:—

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* Phil. Trans. 1855, 179; Chem. Soc. Qu. Jo. ix. 54.

Ferric Nitrate.	Sulphocyanide of Potassium.	Red Salt produced.	Ferric Nitrate.	Sulphocyanide of Potassium.	Red Salt produced.
1 equiv.	3 equiv.	88	1 equiv.	63 equiv.	356
1 "	6 "	127	1 "	99 "	419
1 "	9·6 "	156	1 "	135 "	487
1 "	12·6 "	176	1 "	189 "	508
1 "	16·2 "	195	1 "	243 "	539
1 "	19·2 "	213	1 "	297 "	560
1 "	28·2 "	266	1 "	375 "	587
1 "	46·2 "	318			

The addition of a colourless salt reduced the colour of a solution of ferric sulphocyanide, the reduction increasing in a regularly progressive ratio, according to the mass of the colourless salt.

Similar results were obtained with other ferric salts, viz., with the black gallate, the red meconate and pyromeconate, the blue solution of Prussian blue in oxalic acid, &c., and likewise with the coloured salts of other metals, *e. g.*, the scarlet bromide of gold, the red iodide of platinum, the blue sulphate of copper, when treated with different chlorides, &c.

The amount of fluorescence exhibited by a solution of acid sulphate of quinine, was found to be affected by the mixture of a chloride, bromide, or iodide, according to the nature and mass of the salt added; and the addition of sulphuric, phosphoric, nitric, and other acids was found to produce a fluorescence in solutions of hydrochlorate of quinine or of sulphate which had been rendered non-fluorescent by the addition of hydrochloric acid. Solutions of horse-chestnut bark, and of tincture of thorn-apple, yielded similar results.

The conclusions to be drawn from Dr. Gladstone's experiments, which afford a complete confirmation of Berthollet's theory, so far at least as relates to the action of substances in solution, are as follows:—

When two or more binary compounds are mixed under such circumstances that all the resulting compounds are free to act and react, each electro-positive element enters into combination with each electro-negative element in certain constant proportions, which are independent of the manner in which the different elements are primarily arranged, and are not merely the resultant of the various strengths of affinity of the several substances for each other, but are dependent also on the mass of each of the substances present in the mixture. All deductions respecting the arrangement of substances in solution, drawn from such empirical rules as that the strongest acid combines with the strongest base, must therefore be fallacious.

An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

This equilibrium of affinities arranges itself in most cases in an appreciably short time; but, in certain instances, the elements do not attain their final state of combination for hours.

Totally different phenomena present themselves where precipitation, volatilization, crystallization, and perhaps other actions occur, simply because one of the substances is thus removed from the field of action, and the equilibrium, which was at first established, is thus destroyed (p. 185).

The reciprocal action of salts in solution has also been examined by Malaguti,* whose method consists in taking two salts, both of which are soluble in water, but only one of which is soluble in alcohol, mixing them in equivalent proportions in water, then pouring the aqueous solution into a large quantity of alcohol, and

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* Ann. Ch. Phys. [3], xxxvii. 198.

analyzing the precipitate, in order to ascertain the quantities of the original salts which have been decomposed. Malaguti concludes from his experiments that, in the mutual action of two salts, if nothing separates from the liquid, the decomposition is most complete when the strongest acid and the strongest base are not originally united in the same salt, and that two experiments of this kind, made in opposite ways, must lead to the same final result; that, for example, when 1 eq. of acetate of baryta is added to 1 eq. of nitrate of lead, the quantities of nitrate of baryta and nitrate of lead ultimately present in the liquid are the same as when 1 eq. nitrate of baryta is mixed with 1 eq. acetate of lead. The greater the quantity of the two salts decomposed in the one case, the smaller will be the quantity decomposed in the other; so that if the quantity of any salt, out of 100 parts, which is decomposed by the action of another salt (always supposing that the whole remains in solution) be called the *coefficient of decomposition*, the law of the reaction is, that the sum of the coefficients of decomposition in the two cases is always equal to 100. For example: if 1 at. sulphate of potash and 1 at. acetate of soda act upon each other, and $\frac{64}{100}$ of the original quantity of sulphate of potash remain in solution as such, the coefficient of decomposition is 36. The numerical values of the coefficients of decomposition, determined in several cases by the method above described, are given in the following table:—

Salts.	Coefficient of Decomposition.	Salts.	Coefficient of Decomposition.
Acetate of potash Nitrate of lead	92·0	Acetate of lead Nitrate of potash	9·0
Chloride of potassium Sulphate of zinc	84·0	Chloride of zinc Sulphate of potash	17·6
Acetate of baryta Nitrate of lead	77·0	Acetate of lead Nitrate of baryta	22·0
Chloride of sodium Sulphate of zinc	72·0	Chloride of zinc Sulphate of soda	29·0
Acetate of baryta Nitrate of potash	72·0	Acetate of potash Nitrate of baryta	27·0
Acetate of potash Nitrate of strontia	67·0	Acetate of strontia Nitrate of potash	36·0
Acetate of strontia Nitrate of lead	65·5	Acetate of lead Nitrate of strontia	33·0
Acetate of potash Sulphate of soda	62·0	Acetate of soda Nitrate of potash	36·5
Chloride of potassium Manganous sulphate	58·0	Manganous chloride Sulphate of potash	42·5
Chloride of potassium Sulphate of magnesia	56·0	Chloride of magnesium Sulphate of potash	43·0
Chloride of sodium Sulphate of magnesia	54·5	Chloride of magnesium Sulphate of soda	45·8

In all these cases, except one, the coefficients of decomposition are greatest when the strongest acid and the strongest base are not originally united in the same salt. The exceptional case is presented by the mixture of nitric acid, acetic acid, potash, and baryta, in which the greatest coefficient of decomposition is obtained when the nitric acid is at first united, not with the baryta, but with the potash. A similar result was obtained by the action of potash on nitrate of baryta, and of baryta on nitrate of potash, wood-spirit being used as the precipitating agent instead of alcohol. The coefficient of decomposition was 6·9 in the former case, and 93·6 in the latter.

It is not easy to determine how far the particular numerical results of these experiments were influenced by the presence of the alcohol; but as its action was the same in both cases of each pair of experiments, the results certainly justify the conclusion that the two salts, when mixed, resolve themselves into four; that the partition takes place in a definite manner; and that the proportions of the resulting salts are independent of the manner in which their elements were originally combined.

Experiments bearing on the same point, have also been published by Margueritte,* who finds that two salts in solution mutually decompose each other, even when one of them is already the least soluble of the four salts that may be produced from the two acids and the two bases present. A saturated solution of chlorate of potash, to which chloride of sodium is added, becomes capable of dissolving an additional quantity of chlorate of potash, showing that a portion of the chlorate has been decomposed, and a more soluble salt formed. Chloride of ammonium is precipitated from its saturated aqueous solution on addition of a small quantity of nitrate of ammonia; but the previous addition of chlorate of potash prevents the precipitation; whence it would appear that the chlorate of potash and chloride of ammonium are partially converted into chlorate of ammonia and chloride of potassium. The precipitation of sulphate of lime from its aqueous solution by alcohol, is prevented by the presence of the nitrates or chlorides of potassium, sodium, or ammonium, evidently because a portion of the sulphate is converted into nitrate or chloride. A solution of chloride of ammonium dissolves the carbonates of baryta, strontia, and lime more readily than pure water, because it partially converts them into chlorides, the liquid at the same time acquiring an alkaline reaction, in consequence of the formation of carbonate of ammonia.

The decomposition of insoluble by soluble salts affords a striking instance of the tendency of atoms to interchange, and of the influence of mass on chemical action. According to H. Rose,† sulphate of baryta is completely decomposed by boiling with solutions of alkaline carbonates, provided that each equivalent of sulphate of baryta is acted upon by at least 15 eq. of the alkaline carbonate. If 1 eq. of sulphate of baryta is boiled with only 1 eq. of carbonate of potash, only $\frac{1}{9}$ of it is decomposed, and only $\frac{1}{11}$ by boiling with 1 eq. of carbonate of soda, further decomposition being prevented by the presence of the alkaline sulphate already formed. If, however, the liquid be decanted after a while, the residue boiled with a fresh portion of the alkaline carbonate, and these operations repeated several times, complete decomposition is effected. Carbonate of baryta is converted into sulphate by the action of an aqueous solution of sulphate of potash or soda, even at ordinary temperatures. Solution of carbonate of ammonia does not decompose sulphate of baryta either at ordinary or at higher temperatures; carbonate of baryta is not decomposed by sulphate of ammonia at ordinary temperatures, but easily on boiling. Sulphate of baryta is not decomposed by boiling with caustic potash-solution, provided the carbonic acid of the air be excluded; but by fusion with hydrate of potash, it is decomposed, with formation of carbonate of baryta, because the carbonic acid of the air cannot then be completely excluded. Hydrochloric and nitric acids, left in contact at ordinary temperatures with sulphate of baryta, either crystallized or precipitated, dissolve only traces of it; at the boiling heat, a somewhat larger quantity is dissolved, and the solution forms a cloud, both with a dilute solution of chloride of barium and with dilute sulphuric acid. Sulphate of strontia is dissolved by hydrochloric acid at ordinary temperatures, sufficiently to form a slight precipitate with dilute sulphuric acid, and with chloride of strontium. Sulphate of lime treated with hydrochloric acid, either cold or boiling, yields a liquid in which a precipitate is formed, after a while, by dilute sulphuric acid, but not by chloride of calcium.

Sulphate of strontia and sulphate of lime are completely decomposed by solutions of the alkaline carbonates and bicarbonates at ordinary temperatures, and more quickly on boiling, even if considerable quantities of an alkaline sulphate are added to the solution: the decomposition is also effected by carbonate of

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* Compt. rend. xxxviii. 304.

† Pogg. Ann. xciv. 481; xcv. 96, 284.

ammonia, even at ordinary temperatures. The carbonates of strontia and lime are not decomposed by solutions of the sulphates of potash or soda at any temperature; sulphate of ammonia does not decompose them at ordinary temperatures, but readily with the aid of heat.

Sulphate of lead is completely converted into carbonate by solutions of the alkaline carbonates and bicarbonates, even at ordinary temperatures; the neutral carbonates, but not the bicarbonates, then dissolving small quantities of oxide of lead. Carbonate of lead is not decomposed by solutions of the alkaline sulphates, either at ordinary temperatures or or on boiling.

Chromate of baryta is decomposed at ordinary temperatures by solutions of the neutral alkaline carbonates, and much more easily by boiling with excess of an alkaline bicarbonate. When equivalent quantities of the chromate of baryta and carbonate of soda are boiled with water, $\frac{1}{7}$ of the whole is decomposed; when the same quantities of the salts are fused together, and the mass treated with water, only $\frac{1}{21}$ of the baryta-salt is decomposed. Carbonate of baryta is completely converted into chromate by digestion with a solution of an alkaline monochromate; and the decomposition of chromate of baryta by alkaline carbonates, even at the boiling heat, is completely prevented by the presence of a certain quantity of an alkaline monochromate.

Seleniate of baryta is easily and completely decomposed by solutions of alkaline carbonates, even at ordinary temperatures: this salt is somewhat soluble in water, and more readily in dilute acids.

Oxalate of lime is decomposed by alkaline carbonates even at ordinary temperatures; but to effect complete decomposition the liquid must be frequently decanted and renewed. The decomposition takes place rapidly at the boiling heat; but in all cases it is completely prevented by the presence of a certain quantity of a neulate alkaline oxalate. When the salts are mixed in equivalent proportions, $\frac{2}{17}$ of the oxalate of lime are decomposed at ordinary temperatures, and $\frac{5}{8}$ on boiling. Carbonate of lime is partially converted into oxalate by the action of a solution of neutral oxalate of potash at ordinary temperatures, and more quickly on boiling; — but the decomposition is never complete, even when the liquid is frequently decanted and renewed. — Oxalate of lead is completely converted into carbonate at ordinary temperatures by the solution of an alkaline carbonate, a small portion of the carbonate of lead dissolving in the liquid. (Rose).

The preceding experiments exhibit in a striking manner the influence of difference of solubility in determining the order of decomposition. Sulphate of baryta is less soluble than the carbonate, and, accordingly, carbonate of baryta is more readily decomposed by alkaline sulphates, than the sulphate by alkaline carbonates. Precisely the contrary relations are exhibited by the sulphates and carbonates of strontia* and lime, both as regards solubility and order of decomposition. On the other hand, oxalate of lime is less soluble than the carbonate, and yet its decomposition by alkaline carbonates takes place more easily than the opposite reaction: in this case, the order of decomposition appears rather to be determined, as in Malaguti's experiments, by the tendency of the strongest acid to unite with the strongest base.

The effect of a soluble sulphate, &c., in arresting the decomposition of the corresponding insoluble salts by alkaline carbonates, is evidently due to its tendency to produce the reverse action: hence the acceleration produced by decanting and renewing the liquid. Some insoluble salts, however, phosphate of lime for example, are never completely decomposed, even by this treatment.

The constant tendency to interchange of atoms, exhibited in the phenomena above described, and, indeed, in all cases of chemical action, suggests the idea

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* According to Fresenius, carbonate of strontia dissolves in 11,862 parts, and the sulphate in 6895 parts of cold water.

that the atoms of all bodies, at least in the fluid state, are in constant motion. We have already seen that the same idea is suggested by the phenomena of heat, and leads to a consistent theory of those phenomena (p. 654). On a similar hypothesis, Professor Williamson proposes to construct a general theory of chemical action.* The fundamental notion of this theory is, that the atoms of all compounds, whether similar or dissimilar, are continually changing places, the interchange taking place more readily as the atoms resemble each other more closely. Thus, in a mass of hydrochloric acid, each atom of hydrogen is supposed not to remain quietly in juxtaposition with the atom of chlorine with which it happens to be first united, but to be continually changing places with other atoms of hydrogen, or, what comes to the same thing, continually becoming associated with other atoms of chlorine. This interchange is not perceptible to the eye, because one molecule of hydrochloric acid is exactly like another. But suppose the hydrochloric acid to be mixed with a solution of sulphate of copper (the component atoms of which are likewise undergoing a change of place), the basylous elements, hydrogen and copper, then no longer limit their change of place to the circle of atoms with which they were at first combined, but the hydrogen and copper likewise change places with each other, forming chloride of copper and sulphuric acid. Thus it is that, when two salts are mixed in solution, and nothing separates out in consequence of their mutual action, the bases are divided between the acids, and four salts are produced. If, however, the analogous elements of the two compounds are very dissimilar, and, consequently, interchange but slowly, it may happen that the stronger acid and the stronger base remain almost entirely together, leaving the weaker ones combined with each other. This is strikingly seen in a mixture of sulphuric acid (sulphate of hydrogen) and borate of soda, which soon becomes almost wholly converted into sulphate of soda and free boracic acid (borate of hydrogen).

Now suppose that, instead of sulphate of copper, sulphate of silver is added to the hydrochloric acid. At the first moment the interchange of elements may be supposed to take place as above, and the four compounds, ꞨƟ_4H_2 ꞨƟ_4Ag_2, ClH, and ClAg, to be formed; but the last, being insoluble, is immediately removed by precipitation; the remaining elements then act upon each other in the same way, and this action goes on till all the chlorine or all the silver is removed in the form of chloride of silver; if the original compounds are mixed in exactly equivalent proportions, the final result is the formation of only two salts, viz., in this case, ꞨƟ_4H_2 and ClAg. A similar result is produced when one of the products of the decomposition is volatile at the existing temperature, as when hydrate or carbonate of soda is boiled with chloride of ammonium.

This theory affords a simple explanation of the action of sulphuric acid upon alcohol, whereby sulphovinic acid (sulphate of ethyl and hydrogen) is first formed, and afterwards, at a certain temperature, ether and water are eliminated (p. 182). When alcohol, $\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{Ɵ}$, and sulphuric acid, $\left.\begin{matrix}H\\H\end{matrix}\right\}\text{ꞨƟ}_4$, are mixed together, the interchange between the atoms of ethyl in the former and of hydrogen in the latter gives rise to the formation of sulphovinic acid and water: —

$$\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}\text{ꞨƟ}_4 = \left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{ꞨƟ}_4 + \left.\begin{matrix}H\\H\end{matrix}\right\}\text{Ɵ}.$$

But the change does not stop here, for the sulphovinic acid thus produced, meeting with fresh molecules of alcohol, exchanges its ethyl for the hydrogen of the alcohol, producing ether and sulphuric acid: —

$$\left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{ꞨƟ}_4 + \left.\begin{matrix}\text{Ꞓ}_2H_5\\H\end{matrix}\right\}\text{Ɵ} = \left.\begin{matrix}\text{Ꞓ}_2H_5\\\text{Ꞓ}_2H_5\end{matrix}\right\}\text{Ɵ} + \left.\begin{matrix}H\\H\end{matrix}\right\}\text{ꞨƟ}_4.$$

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* Chem. Soc. Qu. J., iv. 110.

The sulphuric acid is thus restored to its original state, and is ready to act upon fresh quantities of alcohol; so that if alcohol be allowed to run into the mixture in a constant stream, the temperature being kept within certain limits (between 140° and 160° C.), the process goes on without interruption, ether and water continually distil over, and the same quantity of sulphuric acid suffices for the etherification of an unlimited quantity of alcohol. This is the peculiarity of the process; it has given rise to a variety of explanations; in fact, the process of etherification has long been a battle-ground of chemical theories.* The discussion of these various theories would be foreign to the present purpose; it is sufficient to remark that the hypothesis of atomic interchange affords a ready explanation of the most obscure point in the reaction, viz., the formation and decomposition of sulphovinic acid following each other continuously, without any change of temperature or other determining cause. If it be admitted that the atoms of ethyl and hydrogen in the mixture are continually interchanging in all possible ways, this series of alternate actions follows as a necessary consequence.

The formation of ether by the mutual action of sulphovinic acid and alcohol is also analogous to its production by the action of iodide of ethyl on potassium-alcohol (p. 699):—

$$\left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \mathrm{K}\end{matrix}\right\}\text{Ɵ} + \text{Ꞓ}_2\mathrm{H}_5\mathrm{I} = \left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \text{Ꞓ}_2\mathrm{H}_5\end{matrix}\right\}\text{Ɵ} + \mathrm{KI}.$$

The same view is corroborated by the fact recorded by Williamson, in the paper above quoted, that sulphamylic acid (sulphate of amyl and hydrogen) distilled with common alcohol, yields an ether containing both ethyl and amyl:—

$$\left.\begin{matrix}\text{Ꞓ}_5\mathrm{H}_{11}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\text{Ɵ}_4 + \left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \mathrm{H}\end{matrix}\right\}\text{Ɵ} = \left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \text{Ꞓ}_5\mathrm{H}_{11}\end{matrix}\right\}\text{Ɵ} + \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\text{Ɵ}_4;$$

and that the same compound is obtained by distilling a mixture of vinic and amylic alcohols with sulphuric acid; also with the fact discovered by Chancel, that sulphovinate of potassium distilled with potassium-alcohol, yields ether:—

$$\left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \mathrm{K}\end{matrix}\right\}\mathrm{S}\text{Ɵ}_4 + \left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \mathrm{K}\end{matrix}\right\}\text{Ɵ} = \left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \text{Ꞓ}_2\mathrm{H}_5\end{matrix}\right\}\text{Ɵ} + \left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{S}\text{Ɵ}_4;$$

and that the same salt distilled with methylate of potassium, $\text{Ꞓ}\mathrm{H}_3\mathrm{K}\text{Ɵ}$, yields methamylic ether, $\left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_5\\ \text{Ꞓ}\mathrm{H}_3\end{matrix}\right\}\text{Ɵ}$.

The idea of atomic motion is in accordance with physical as well as chemical phenomena. To suppose that rest, rather than motion, is the normal state of the particles of matter, is at variance with all that we know of the effects of light, heat, and electricity. In the heat-theory of Clausius, (p. 653), the particles of bodies are supposed to be affected with progressive, as well as with rotatory and vibratory movements; and this same hypothesis of progressive movement which, of course, implies change of relative position among the particles, affords, as already stated, a ready explanation of certain chemical reactions, otherwise somewhat obscure. It is worth while to observe that, in the heat-theory of Clausius, the progressive motion of the particles is supposed to exist only in the liquid and gaseous states, the particles of solid bodies merely performing rotatory and vibratory movements about certain positions of equilibrium. This is quite in accordance with the well-known fact that chemical reaction rarely takes place between solid bodies.

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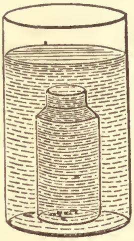
* See the translation of Gmelin's Handbook, vol. viii. pp. 231—237.

DIFFUSION OF LIQUIDS.

Intimately connected with the interchange of atoms resulting in chemical decomposition, is the process by which a saline, or other soluble substance, is spread or diffused uniformly through the mass of the solvent; in some cases, indeed, as will presently be seen, the decomposition of salts is greatly facilitated by the tendency of one or more of the products of decomposition to diffuse into the surrounding liquid.

The phenomena of liquid diffusion have been minutely investigated by Mr. Graham.* The apparatus used consisted of a set of phials, of nearly equal capacity, cast in the same mould, and further adjusted by grinding to a uniform size of aperture. The phials were 3·8 inches high, with a neck 0·5 inch in depth, and aperture 1·25 inch wide; capacity to base of neck equal to 2080 grains of water, or between 4 and 5 ounces. For each *diffusion-phial*, a plain glass *water-jar* was also provided, 4 inches in diameter and 7 inches deep. (Fig. 229.)

FIG. 229.



The diffusion-phial was filled with the saline solution, sal-ammoniac for instance, to the base of the neck, or more correctly to a distance of 0·5 inch from the ground surface of the lip. The neck of the phial was then filled up with distilled water, a light float being first placed on the surface of the solution, and care being taken to avoid agitation. After the phial had been placed within the jar, water was poured into the jar, so as to cover the open phial to the depth of an inch, which required about 20 ounces of water. The saline liquid in the phial is thus allowed to communicate freely with the water in the jar. The diffusion is interrupted by placing a small plate of ground glass on the mouth of the phial, and raising the latter out of the jar. The amount of salt diffused, called the *diffusion-product*, or *diffusate*, is ascertained by evaporating the water in the jar to dryness, or, in the case of chlorides, by precipitating with nitrate of silver.

The results of several series of experiments made in this manner are given in the following Table, the second column of which shows the quantity of salt in 100 parts of the solution; the third, the time of diffusion; the fourth, the temperature, on the Fahrenheit scale; the fifth, the quantity of salt diffused:—

DIFFUSION OF SALINE SOLUTIONS.

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Hydrochloric acid	1	5	51°	7·41
	2	5	51	15·04
	2	5	59·7	16·55
	4	5	51	30·72
	8	5	51	67·68
Hydriodic acid	2	5	51	15·11
Hydrobromic acid	2	5	59·7	16·58
Bromine	0·864	10	60·1	5·84
Hydrocyanic acid	1.766	5	64·2	11·68
Hydrated nitric acid (NO_6H)	1	5	51·2	6·99
	2	5	51·2	14·74
	4	5	51·2	28·76
	8	5	51·2	57·92

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* Phil. Trans. 1850, pp. 1, 805; Chem. Soc. Qu. J. ii. 60, 257; iv. 83.

Diffusion of Saline Solutions — *continued.*

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Hydrated sulphuric acid (SO_4H)	1	10	49·7°	8·69
	2	10	49·7	16·91
	4	10	49·7	33·89
	8	10	49·7	68·96
Chromic acid	1·762	10	67·3	19·78
Acetic acid ($C_4H_4O_4$).......	2	10	48·8	11·31
	4	10	48·8	22·02
	8	10	48·8	41·80
Sulphurous acid...........................	1	10	68·1	8·09
	2	10	68·1	16·96
	4	10	68·1	33·00
	8	10	68·1	66·38
Ammonia....................................	1	4.04	63·4	4·93
	2	4·04	63·4	9·59
	4	4·04	63·4	19·72
	8	4·04	63·4	41·22
Alcohol.......................................	2	10	48·7	8·62
	4	10	48·7	16·12
	8	10	48·7	35·50
Nitrate of baryta............................	1	11·43	64·1	7·72
	2	11·43	64·1	15·04
	4	11·43	64·1	29·60
	8	11·43	64·1	54·50
Nitrate of strontia	0.82	11·43	51·5	5·59
Nitrate of lime	1	11·43	64·1	7·66
	2	11·43	64·1	15·01
	4	11·43	64·1	29·04
	8	11·43	64·1	55·10
Acetate of baryta	1	16·17	53·5	7·50
Acetate of lead................................	1	16·17	53·1	7·84
Chloride of barium..........................	1	8·57	6·3	6·32
	2	8·57	6·3	12·07
	4	8·57	6·3	23·96
	8	8·57	6·3	45·92
Chloride of strontium......................	1	8·57	6·3	6·09
	2	8·57	6·3	11·66
	4	8·57	6·3	23·56
	8	8·57	6·3	44·46
Chloride of calcium.........................	1	11·43	63·8	7·92
	2	11·43	63·8	15·35
	4	11·43	63·8	30·78
	8	11·43	63·8	61·56
	1	11·43	50·8	6·51
Chloride of manganese.....................	1	11·43	50·8	6·63
Nitrate of magnesia	1	11·43	50·8	6·49
Nitrate of copper............................	1	11·43	50·8	6·44
Chloride of zinc................................	1	11·43	50·8	6·29
Chloride of magnesium	1	11·43	50·8	6·17
Cupric chloride.................................	1	11·43	50·8	6·06
Ferrous chloride	1	11·43	53·5	6·30
Sulphate of magnesia.......................	1	16·17	65·4	7·31
	2	16·17	65·4	12·79
	4	16·17	65·4	23·46
	8	16·17	65·4	42·82
	8	16·17	62·8	42·66
	16	16·17	62·8	75·06
	24	16·17	62·8	102·04
Sulphate of zinc	1	16·17	65·4	6·67
	2	16·17	65·4	12·22
	4	16·17	65·4	23·12
	8	16·17	65·4	42·26
	8	16·17	62·8	39·62
	16	16·17	62·8	74·40
	24	16·17	62·8	101·42

Diffusion of Saline Solutions—*continued.*

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Sulphate of alumina	1	16·17°	65·4	5·48
	2	16·17	65·4	10·21
	4	16·17	65·4	19·28
	8	16·17	65·4	33·52
Nitrate of silver	2	7	63·4	13·61
	4	7	63·4	26·34
	8	7	63·4	51·88
Nitrate of soda	2	7	63·4	12·35
	4	7	63·4	23·56
	8	7	63·4	47·74
Chloride of sodium	1	7	63·4	6·32
	2	7	63·4	12·37
	4	7	63·4	24·96
	8	7	63·4	48·44
	2	7	63·4	12·14
Iodide of sodium	2	7	59·8	12·18
Bromide of sodium	2	7	59·8	12·14
Chloride of potassium	2	5·716	59·8	12·24
Bromide of potassium	2	5·716	59·8	12·46
Iodide of potassium	2	5·716	59·8	12·51
Chloride of ammonium	1	5.716	59·8	5·99
Bicarbonate of potash	1	8·08	68·2	7·23
	2	8·08	68·2	14·05
	4	8·08	68·2	26·72
	8	8·08	68·2	52·01
Bicarbonate of ammonia	1	8·08	68·2	6·91
	2	8·08	68 2	13·65
	4	8·08	68·2	27·00
	8	8·08	68·2	50·10
Bicarbonate of soda	1	9·87	68·2	7·31
	2	9·87	68·2	13·81
	4	9·87	68·2	26·70
	8	9·87	68·2	52·38
Hydrate of potash	1	4·04	63·3	6·56
	2	4·04	63·3	12·84
	4	4·04	63·3	25·04
	8	4·04	63·3	52 24
Hydrate of soda	1	4·95	63·2	5·81
	2	4·95	63·2	11·09
	4	4·95	63·2	20·86
	8	4·95	63·2	40·44
Carbonate of potash	1	8·08	63·6	6·13
	2	8·08	63·6	11·92
	4	8·08	63·6	22·88
	8	8·08	63·6	45·44
Carbonate of soda	1	9·9	63·4	6·02
	2	9·9	63·4	11·70
	4	9·9	63·4	21·42
	8	9·9	63·4	39·74
Sulphate of potash	1	8·08	60·2	6·16
	2	8·08	60·2	11·60
	4	8·08	60·2	22·70
	8	8·08	60·2	43·92
Sulphate of soda	1	9·9	59·9	6·33
	2	9·9	59 9	12·00
	4	9·9	59·9	21·96
	8	9·9	59·9	41·38
Sulphite of potash	2	8·08	59·5	11·63
Sulphite of soda	2	9 9	59·5	11·83
Hyposulphite of potash	2	8·08	59·7	12·37
Hyposulphite of soda	2	9·9	59·9	11·89
Sulphovinate of potash	2	8·08	59·7	12·60
Sulphovinate of soda	2	9·9	59·5	13·03

Diffusion of Saline Solutions—*continued.*

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Oxalate of potash	1	8·08	59·9°	6·20
	2	8·08	59·9	12·17
	4	8·08	59·9	23·04
	8	8·08	59·9	42·82
Oxalate of soda	1	9·9	59·9	6·24
Acetate of potash	1	8·08	60·2	6·44
	2	8·08	60·2	12·52
	4	8·08	60·2	23·44
	8	8·08	60·2	47·26
Acetate of soda	1	9·9	59·5	6·67
	2	9·9	59·5	12·46
	4	9·9	59·5	25·04
	8	9·9	59·5	48·04
Tartrate of potash	2	8·08	59·9	10·96
Tartrate of soda	2	9·9	59·5	10·65
Hydrochlorate of morphine	2	11·43	64·1	11·60
Hydrochlorate of strychnine	2	11·43	64·1	11·49

These experiments, and a number of others made in a similar manner, lead to the following general conclusions:—

1. Different salts, in solutions of equal strength, diffuse unequally in equal times.

2. With each salt, the rate of diffusion increases with the temperature, and at any given temperature, is proportionate to the strength of the solution, at least when the quantity of salt dissolved does not exceed 4 or 5 per cent.

3. There exist classes of equidiffusive substances which coincide in many cases with the isomorphous groups, but are, on the whole, more comprehensive than the latter. Thus, the same rate of diffusion is exhibited by hydrochloric, hydrobromic, and hydriodic acid; by the chlorides, iodides, and bromides of the alkali-metals; by the nitrates of baryta, strontia, and lime; the sulphates of magnesia and zinc, &c. &c.

4. For several groups of salts it is found that the squares of the times of equal diffusion, from solutions of the same strength, stand to one another in a simple numerical relation. Thus, the diffusate from a solution of nitrate of potash, in 7 days, was equal to that obtained from an equally strong solution of carbonate of potash, in 9·9 days, numbers which are to one another as $1 : \sqrt{2}$. Similar results were obtained with 2 per cent. solutions of nitrate and sulphate of potash, equal diffusates of the two being obtained in 3·5 and 4·95 days, in 7 and 9·9 days, and in 10·5 and 14·85 days; also, with hydrate and nitrate of potash, and with nitrate and carbonate of soda. The times of equal diffusion of 1 per cent. solutions of chloride of ammonium and chloride of sodium, were to one another as $\sqrt{2} : \sqrt{3}$. Now, according to Mr. Graham's experiments (p. 739), the squares of the times of equal diffusion of gases are to one another in the ratio of their densities. Hence, by analogy, it may be inferred that the molecules of these several salts, as they exist in solution, possess densities which are to one another as the squares of the times of equal diffusion. Thus, the *solution-densities* of sulphate, nitrate, and hydrate of potash, are to one another as the numbers 4, 2, and 1. These solution-densities appear to relate to a kind of molecules different from the chemical atoms, and the weights of which are either equal, or bear to one another a simple numerical relation.

The diffusion of a salt into the solution of another salt takes place with nearly the same velocity as into pure water; at least, when the solutions are dilute. Mr Graham has shown that the diffusion of a 4 per cent. solution of carbonate of soda, is not sensibly affected by the presence of 4 per cent. of sulphate of soda in the liquid atmosphere; nor that of a 4 per cent. solution of nitrate of potash, by the same proportion of nitrate of ammonia. The presence of 4 per cent. of sulphate of soda reduced the diffusion of carbonate of soda by only $\frac{1}{8}$ of the whole. In stronger solutions the retardation would probably be greater. There is, indeed, reason to believe that the phenomena of liquid diffusion are exhibited in their simplest form only by weak solutions, the effect of concentration, like that of compression in gases, being to produce a departure from the normal character.

The rate of diffusion is, however, materially affected when the liquid atmosphere already contains a portion of the diffusing salt. The consideration of this case leads to the general question of the motion of particles of a dissolved substance in a solution of unequal concentration. The general law which regulates such movements appears to be this:—*The velocity with which a soluble salt diffuses from a stronger into a weaker solution, is proportional to the difference of concentration between two contiguous strata.* This law has not yet been experimentally demonstrated in a sufficient number of cases to establish it completely; but in the case of chloride of sodium, it has been shown to be true by the following experiments of Fick.*

A cylindrical glass tube, open at both ends, was cemented into a vessel completely filled with common salt, the cylindrical space filled up with water, and the whole immersed in a large jar containing water. The apparatus was then left to itself for several weeks, the water in the jar being from time to time taken out and renewed. Now, as the lowest stratum of liquid in the tube, being in contact with undissolved salt, must remain constantly saturated, while the uppermost layer, which is in contact with pure water, contains no salt at all, a certain normal state of diffusion will ultimately establish itself throughout the length of the tube, characterized by the condition, that each horizontal stratum will, in a given time, give up to the stratum immediately above it as much salt as it receives from the one below. When this state is attained, the densities of the successive strata decrease from below upwards in arithmetical progression. This law of decrease was verified experimentally by immersing in the liquid, at various depths, a glass bulb suspended from the arm of a balance, and counterpoised by weights in the opposite scale. This law of decrease, however, is true only with regard to cylindrical columns of liquid, or others, in which the horizontal section is of uniform magnitude. In other cases, the law of decrease of density may be calculated according to the form of the vertical section. In funnel-shaped tubes, Fick has shown that the results of calculation agree with those of experiment.

Now let K denote the quantity of salt which, in the normal state of diffusion, passes in a unit of time through a unit of horizontal section of a cylindrical tube whose height is equal to the unit of length: this quantity is called the *diffusion-coefficient;* also, let Q be the quantity of salt which, in the time t, flows from the mouth of the tube into the water-atmosphere; h, the height of the tube; s, its horizontal section; and d, the density of the liquid at the bottom; then

$$Q = K \,.\, d \,.\, \frac{s}{h}\, t.$$

Hence, with a tube of given dimensions, and a solution of known and constant density at the bottom, the *diffusion-coefficient*, K, of any salt, may be calculated from the quantity Q, diffused out in a given time.

This method has been applied by Fick only in the case of chloride of sodium. It is, in fact, though simple in principle, somewhat inconvenient of application, on account of the long time—at least 14 days—which must elapse before the normal state is attained.

Another method of determining the diffusion co-efficient of a salt has been

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* Phil. Mag. [4], x. 30.

devised by Jolly, and applied in several cases by Beilstein.* The apparatus used consists of a glass tube (fig. 230), about three inches long, bent round at the bottom, and cut off near the bend, so that the level of the orifice is not much more than a millimeter above the bottom of the bend at *a*. The upper end of the tube is slightly drawn out, and closed with a stopper. This tube is filled with a solution of known concentration, and fixed upright within a jar of water, the orifice of the tube being two or three lines below the level of the water. The salt then immediately begins to diffuse into the water, and as the liquid near the orifice becomes diluted, it passes round the bend to the upper part of the tube, its place being supplied by more concentrated liquid from above. With this apparatus, Beilstein has obtained the following diffusion-coefficients (taking that of chloride of potassium for unity), for solutions containing 4 per cent of salt, and at the temperature of 6° C. (10·2° F.).

FIG. 230.

Chloride of potassium	1	Sulphate of potash	0·6987
Nitrate of potash	0·9487	Carbonate of soda	0·5436
Chloride of sodium	0·8337	Sulphate of soda	0·5369
Bichromate of potash	0·7543	Sulphate of magnesia	0·3587
Carbonate of potash	0·7371	Sulphate of copper	0·3440

Beilstein infers from his experiments, that the rate of diffusion is not exactly proportional to the difference of density of two contiguous strata, but increases in a somewhat greater ratio.

Simmler and Wilde† are of opinion that the want of agreement of Beilstein's results with this law arises from a defect in the method of experimenting. Beilstein's calculations, indeed, are based on the supposition that the strength of the solution in the tube (fig. 230), though constantly decreasing, is uniform at any instant of time throughout the entire length; whereas, a little consideration will show that the density near the orifice must be less than that in the larger arm of the tube, and in this arm less than near the bottom of the bend, where the liquid must stagnate to a certain extent. From this source of error, Fick's mode of observation is free. Simmler and Wilde, however, propose other methods, easier of execution than Fick's, and not subject to the necessity of waiting till the normal state of diffusion is established. One of these methods is similar to that adopted by Mr. Graham, excepting that the vessel containing the solution is perfectly cylindrical, a condition which greatly simplifies the calculations; and, instead of being placed at the bottom of the water-jar, is supported on a stand, so as to bring its mouth within a line or two below the surface of the water; the salt, as it diffuses out, is thus made to flow over the sides of the vessel and fall to the bottom, leaving an atmosphere of pure water above. Another method, proposed by the same authors, is to place the saline solution in a vessel having the form of a triangular prism, and determine the variation of density at different depths below the surface by observation of the indices of refraction. The numerical results obtained by these methods have not yet been published.

Mixed salts may be more or less separated by their unequal diffusibility. A solution of 1 part of carbonate of potash and 1 part of carbonate of soda in 10 parts of water, yielded in 19 days at 60° F. a diffusate containing 63·6 parts of carbonate of potash to 36·4 parts of carbonate of soda; the diffusate obtained in 25 days contained the two salts in nearly the same proportion. Sea-water was also partially decomposed by diffusion, the diffusate containing a smaller proportion of magnesia-salts than the residue. The variation of composition in the water of the Dead Sea, at different times of the year, probably arises from the unequal rate of diffusion of the different salts contained in the strong saline liquid into the layer of fresh water brought down to it during the rainy season. (Graham.)

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* Ann. Ch. Pharm. xcix. 165.

† Pogg. Ann. C. 217.

Diffusion is also capable of effecting the decomposition of chemical compounds. From a solution of bisulphate of potash, saturated at 20° C. (68° F.), there were diffused in 50 days, 31·8 parts of bisulphate of potash, and 12·8 parts of hydrated sulphuric acid. A solution of 8 parts of anhydrous alum in 100 parts of water yielded, in 8 days, at 17·9° C. (64·2° F.), a diffusate of 5·3 parts alum and 2·2 parts sulphate of potash. A solution of 1 part of sulphate of potash in 100 parts of lime-water, left to diffuse into lime water for seven days, yielded as a mean result, a diffusate containing 22·67 parts of hydrate of potash, and 77·33 parts of sulphate of potash. A similar experiment with sulphate of soda, yielded a diffusate containing about 12 per cent. of hydrate of soda. The larger quantity of the alkaline hydrate obtained in the first instance, appears to be due to the superior diffusibility of the sulphate of potash, as it can scarcely be supposed that the affinity of potash for sulphuric acid is less than that of soda. The sulphates of potash and soda were also decomposed by carbonate of lime dissolved in carbonic acid water, when the liquid was allowed to diffuse into pure water. The chlorides of potassium and sodium were not sensibly decomposed by lime-water in this manner. When saturated solutions of lime-water and sulphate of lime were mixed in equal volumes, 1 per cent. of chloride of sodium dissolved in the mixture, and the solution left to diffuse into pure water, scarcely a trace of hydrate of soda was obtained; but when the solution of sulphate of lime, with an addition of 2 per cent. of chloride of sodium, was kept at the boiling point for half an hour, and the solution mixed two or three days afterwards with an equal volume of lime-water, and diffused into pure water for 3½ days, the diffusate in three cells was found to contain 0·234 grains hydrate of soda, and 0·371 sulphate of soda. It appears, then, that more than one condition of equilibrium is possible for mixed solutions of sulphate of lime and chloride of sodium. Cold solutions of these salts may be mixed without decomposition, or, without sensible formation of sulphate; but, on heating, this change is induced, and is permanent, sulphate of soda being formed, and continuing to exist in the cold solution; for it is the decomposition of that salt alone by hydrate of lime which appears to yield the diffused hydrate of soda. As the effects of time and temperature are often convertible, it is possible that the same decomposition might take place at ordinary temperatures after a considerable time. "If such be the case, we have an agency in the soil, by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates, for the sulphate of lime, generally present, will convert those chlorides into sulphates. The mode in which the soil of the earth is moistened by rain, is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they find afterwards an atmosphere of nearly pure water, in the moisture which falls last and occupies the surface-stratum of the soil. Diffusion of the salts upwards into the water, with its separations and decompositions, must necessarily ensue. The salts of potash and ammonia, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of lime, particularly as quick-lime is applied for a top-dressing to grass lands." (Graham.*)

PASSAGE OF LIQUIDS THROUGH POROUS SEPTA. OSMOSE.

The force of liquid diffusibility still acts when the two liquids are separated by a porous sheet of animal membrane, or unglazed earthenware; for the pores of such a membrane are occupied by water, and an uninterrupted liquid communication exists between the water on the one side, and the saline solution on the other. Under these circumstances, a flow of liquid takes place, generally, though

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* Chem. Soc. Qu. J. iii. 67.

not always, from the water to the saline solution, so that the quantity of liquid diminishes on one side of the septum, while it increases on the other. This phenomenon was originally designated by the correlative terms, *Endosmose* and *Exosmose;* but it is better expressed by the shorter word *Osmose* (from ὦσμος, impulsion), which includes the two former.

This passage of liquids through porous septa, was first studied by Dutrochet, whose apparatus, called an *endosmometer*, consisted of a narrow glass tube, having a funnel-shaped expansion at the bottom, and closed at that end by a piece of bladder. This tube was filled with a saline solution, and placed in a vertical position, in a jar containing water. The flow of liquid in one direction or the other, was measured by the rise or fall of the liquid in the tube. Dutrochet inferred from his experiments that the velocity of the osmotic current is proportional to the quantity of salt or other solid substance originally contained in the saline solution. The experiments were, however, inexact, because no allowance was made for the alteration of hydrostatic pressure, caused by the rise or fall of liquid in the tube. Vierordt,* who used a modification of Dutrochet's apparatus, in which this source of error was removed, found that the velocity of the current increases with the initial concentration of the solution, but in a lower ratio.

Professor Jolly, of Heidelberg, has examined the osmose of water and saline solutions by a different method. The saline solution containing a known quantity of salt, is contained in a glass tube closed at the bottom with bladder, and plunged into water, which is frequently changed, so as to keep it nearly pure. The tube with its contents is taken out from time to time and weighed, and these operations are repeated till the weight becomes constant, showing that the whole of the salt has passed out from the tube, and nothing but water remains.

In this manner, it is found that a given quantity of any salt which passes through the septum into the water is always replaced by a definite quantity of water. The quantity of water which is thus replaced by a unit of weight of the salt, is called the *endosmotic* (or *osmotic*) *equivalent* of that salt. This quantity varies with the nature of the salt, and with the temperature, increasing as the temperature rises, but it is independent of the density of the solution. At temperatures near 0° C., the endosmotic equivalent of hydrate of potash was found to be 200; of chloride of sodium, between 4·3 and 4·6; of sulphate of soda, between 11 and 12; of neutral sulphate of potash, 12; of acid sulphate of potash, 2·3; and of hydrated sulphuric acid (at 18° C.), 0·35.

These results point to the conclusion, that the osmose between water and saline solutions, consists, not in the opposite passage of two liquid currents, but in the passage of particles of the salt in one direction, and of pure water in the other. This conclusion is strengthened by Mr. Graham's observation, that common salt diffuses into water, through a tin membrane of ox-bladder deprived of its outer muscular coating, at the same rate as when no membrane is interposed.

The flow of water into the saline solution is the only one of the two movements which can be correctly described as a current. This is, in fact, the true osmose, and depends essentially on the action of the membrane or other porous septum; for the quantity of water which thus passes into the solution, is often much greater than would be introduced by mere liquid diffusion, amounting in some cases to several hundred times that of the salt displaced.

This action of the septum has been explained in various ways. By Dutrochet and others, it was attributed to capillarity; but this force is quite insufficient to account for the great inequality of ascension which different liquids exhibit in the osmotic apparatus; in fact, Mr. Graham has shown, that solutions of the most different character exhibit very nearly equal ascension in tubes of equal diameter.

Osmose has likewise been attributed to the unequal absorption of the two liquids by the porous septum. Suppose the septum to be of such a nature as to

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* Pogg. Ann. lxxiii. 519.

absorb only one of the liquids, the water for instance. The water will then penetrate the septum, and coming in contact with the saline solution, will diffuse into it. More water will then be absorbed, and subsequently diffused, and thus a continuous current will be set up. If both liquids are absorbed by the septum, but in different degrees, and each is capable of diffusing into the other, like water and alcohol, the result will be the formation of two unequal currents in opposite directions. Water is absorbed by animal membrane much more rapidly than most other liquids, and accordingly, when a septum of this kind is used, the direction of the current is in most cases from the water to the other liquid. According to Liebig, a given weight of dried ox-bladder absorbs in the same time, 200 volumes of water, 133 vols. of a saturated solution of common salt, 38 vols. of alcohol of the strength of 84 per cent., and 17 vols. of bone-oil. When water and alcohol are separated by an animal membrane, the quantity of water which passes into the alcohol, is greater than the quantity of alcohol which passes into the water; but when the same liquids are divided by a thin film of collodion, which absorbs alcohol more quickly than water, the contrary effect is produced.

On the other hand, the numerous experiments recently made by Mr. Graham,* lead to the conclusion, that osmose depends essentially on the chemical action of the liquid on the septum. These experiments were made partly with porous mineral septa, partly with animal membrane. The earthenware osmometer consisted of the porous cylinders employed in voltaic batteries, about five inches in depth, surmounted by a glass tube 0·6 inch in diameter, attached to the mouth of the cylinder by means of a cap of gutta percha. The cylinder was filled to the base of the glass tube with a saline solution, and immediately placed in a jar of distilled water; and as the fluid within the instrument rose during the experiment, water was added to the jar to equalize the pressure. The rise (or fall) of the liquid in the tube was very regular, as observed from hour to hour, and the experiment was generally terminated in five hours. From experiments made on solutions of every variety of soluble substance, it appeared that the rise or osmose, is quite insignificant with neutral organic substances in general, such as sugar, alcohol, urea, tannin, &c.; so likewise with neutral salts of the earths and ordinary metals, with the chlorides and nitrates of potassium and sodium, and with chloride of mercury. A more sensible but still very moderate osmose is exhibited by hydrochloric, nitric, acetic, sulphurous, citric, and tartaric acids. These are surpassed by the stronger mineral acids, such as sulphuric and phosphoric, and by sulphate of potash, which are again exceeded by salts of potash and soda possessing a decided acid or alkaline reaction, such as binoxalate of potash, phosphate of soda, or the carbonates of potash and soda. The highly osmotic substances were also found to act with most advantage in small proportions, producing, in fact, the largest osmose in the proportion of one-quarter per cent. dissolved. (See page 749). The same substances are likewise always chemically active bodies, and possess affinities which enable them to act on the material of the earthenware septum. Lime and alumina were always found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow. Septa of other materials, such as pure carbonate of lime, gypsum, compressed charcoal, and tanned sole-leather, although not deficient in porosity, gave no osmose, apparently because they are not chemically acted on by the saline solutions.

Similar results were obtained with septa of animal membrane. Ox-bladder was found to act with much greater strength and regularity when divested of its outer muscular coat. Cotton calico, impregnated with liquid albumen, and afterwards heated to coagulate the albumen, formed an excellent septum, resembling membrane in every respect. The osmometer (fig. 231) used in these experiments was arranged like the original instrument of Dutrochet; but the membrane was supported by a plate of perforated zinc, and the tube was of considerable diameter,

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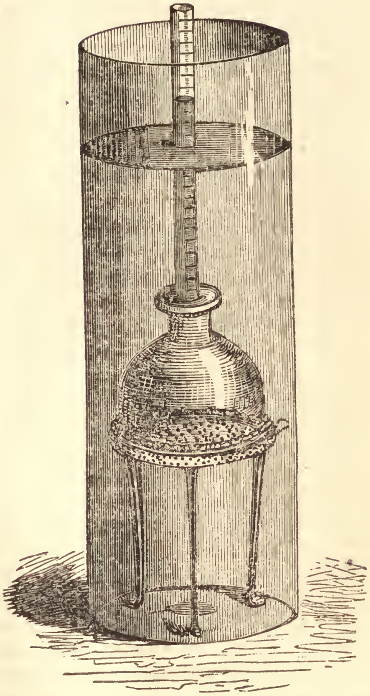
* Phil. Trans. 1855, 177; Chem. Soc. Qu. J., viii. 43.

viz., one-tenth of that of the mouth of the bulb, or of the disc of membrane exposed to the liquids.

FIG. 231.



Osmose in membrane presents many points of similarity to that in earthenware. The membrane is constantly undergoing decomposition, and its osmotic action is exhaustible. Salts and other substances capable of determining a large osmose, are all chemically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as chloride of sodium, possess only a low degree of action, or are wholly inert. The active substances are also most efficient in small proportions.* With a solution containing $\frac{1}{10}$ per cent. of carbonate of potash, the rise in the osmometer was 167 millimeters; and with 1 per cent. of the same salts, 206 millimeters in five hours. With another membrane and a stronger solution, the rise was 863 millimeters, or upwards of 38 inches, in the same time. To induce osmose, the chemical action on the membrane must be different on the two sides, and apparently not in degree only, but in kind, viz., an alkaline action on the albuminous substance of the membrane on the one side, and an acid action on the other. The water appears always to accumulate on the alkaline or basic side of the membrane. Hence, with an alkaline salt, such as carbonate of soda, in the osmometer, and water outside, the flow is inwards; but with an acid in the osmometer, there is negative osmose, or the flow is inwards, the liquid then falling in the tube. The chlorides of barium, sodium, and magnesium, and similar neutral salts, are wholly indifferent, or appear to act merely in a subordinate manner to some other active acid or basic substance, which may be present in the solution or the membrane in the most minute quantity. Salts which admit of division into a basic salt and free acid, exhibit an osmotic activity of the highest order, *e. g.*, the acetate and various other salts of alumina, ferric oxide and chromic oxide, dichloride of copper, protochloride of tin, nitrate of lead, &c. The acid travels outwards by diffusion, superinducing a basic condition of the inner surface of the membrane, and an acid condition of the outer surface, the most favourable condition for a high positive osmose. Again, the bibasic salts of potash and soda, such as the sulphate and tartrate, though strictly neutral in properties, begin to exhibit a positive osmose, in consequence, perhaps, of their resolution into an acid supersalt and free alkaline base.

The following table exhibits the osmose of substances of all classes through membrane, the degree being a rise or fall of one millimeter:—

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* The action increases with the strength of the solution up to a certain point, as the above examples show (see also p. 748). With stronger solutions the pores of the membrane probably become stopped up with particles of salt, and the action consequently diminishes.

Osmose of 1 per Cent. Solutions in Membrane.

	Degrees.
Oxalic acid	— 148
Hydrochloric acid (0·1 per cent.)	— 92
Terchloride of gold	— 54
Bichloride of tin	— 46
Bichloride of platinum	— 30
Chloride of magnesium	— 3
Chloride of sodium	+ 2
Chloride of potassium	18
Nitrate of soda	2
Nitrate of silver	34
Sulphate of potash	21 to 60
Sulphate of magnesia	14
Chloride of calcium	20
Chloride of barium	21
Chloride of strontium	26
Chloride of cobalt	26
Chloride of manganese	34
Chloride of zinc	+ 54
Chloride of nickel	88
Nitrate of lead	125 to 211
Nitrate of cadmium	137
Nitrate of uranium	234 to 458
Nitrate of copper	204
Chloride of copper	351
Protochloride of tin	289
Protochloride of iron	435
Chloride of mercury	121
Mercurous nitrate	356
Mercuric nitrate	476
Ferric acetate	194
Acetate of alumina	280 to 393
Chloride of aluminium	540
Phosphate of soda	311
Carbonate of potash	439

The osmotic action of carbonate of potash and other alkaline salts is interfered with in an extraordinary manner by the presence of chloride of sodium, being reduced to almost nothing by an equal proportion of that salt. The moderate positive osmose of sulphate of potash is converted into a very sensible negative osmose by the presence of the merest trace of a strong acid, while the positive osmose of the same salt is singularly promoted by a small proportion of alkaline carbonate: thus a 1 per cent. solution of sulphate of potash gives an osmose of 21 degrees, but the addition of 0·1 per cent. of carbonate of potash raises it to between 254 and 264 degrees. (Graham.)

If a glass tube, bent in the form of a siphon, and having its shorter leg closed with bladder, be partially filled with salt-water, the shorter leg then immersed in a vessel of pure water, and mercury poured into the longer leg, so that its pressure may act in opposition to the force with which the water tends to enter the saline solution through the bladder, it will be found that, when the column of mercury attains a certain height, the two liquids will mix without change of volume, the force of the osmotic current being then exactly balanced by the weight of the mercurial column. In this way the mechanical force of the osmotic current may be measured. (Liebig.)

Osmose appears to play an important part in the functions of life. We have seen that it is peculiarly excited by dilute saline solutions, such as the animal and vegetable juices are, and that the acid or alkaline property which these juices possess is another favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such solutions seems therefore almost inevitable.

In osmose there is also a remarkably direct substitution of one of the great forces of nature by its equivalent in another force, the conversion, namely, of chemical action into mechanical power. Viewed in this light, the osmotic injection of fluids may, perhaps, supply the deficient link which intervenes between chemical decomposition and muscular movement. The ascent of the sap in plants appears to depend upon a similar conversion of chemical, or, at least, molecular action into mechanical force. The juices of plants are constantly permeating the coatings of the superficial vessels in the leaves and other organs; and these evaporating into the air, a fresh portion of liquid is then absorbed by the membrane and evaporates; and thus a regular upward current is established, by which the sap is transferred from the roots to the highest parts of the tree. In a similar manner, the evaporation constantly taking place from the skin and lungs of animals, causes a continuous flow of the animal juices from the interior towards the surface.

DIFFUSION OF GASES THROUGH POROUS SEPTA.

It appears from Mr. Graham's experiments (p. 88), that the rates of diffusion of gases through porous diaphragms, such as dry gypsum, cork, unglazed earthenware, or bladder, are to one another in the inverse ratio of the squares of their densities, the law being, in fact, the same as that of the *effusion* of the same gases into a vacuum through minute apertures in a metal plate (p. 83). Bunsen has arrived at a different conclusion.* He finds, for example, that when a tube containing hydrogen is closed by a dry gypsum diaphragm, and a current of oxygen passed rapidly over the diaphragm, so that the hydrogen may diffuse into an infinite atmosphere of oxygen, the volume of oxygen which enters the tube is to the volume of hydrogen which issues from the tube, as 1 : 3·345, this ratio remaining constant during the whole time of the diffusion. The law of the inverse square roots of the densities would give 1 : 4. Again, when oxygen was made to pass through stucco into oxygen, and hydrogen into hydrogen, by difference of pressure, it was found that, under the same pressure, the rate of issue of the oxygen was to that of the hydrogen as 1 : 2·73 instead of 1 : 4. These differences are too great to be accounted for by error of observation; they probably arise from the circumstance, that Graham's experiments were made with thin diaphragms, whereas Bunsen used diaphragms of considerable thickness,† in which case, the rates of diffusion would approximate to the rates of transpiration (p. 85) rather than to those of effusion. The rate of transpiration through a mass of porous stucco was ascertained by Mr. Graham to be the same as through capillary tubes, namely, 1 volume of oxygen to 2·3 volumes of hydrogen. In the interior of a considerable mass of stucco, with hydrogen on one side and oxygen on the other, the stucco acts as a vessel, a partial vacuum being formed in its centre. To this point, both oxygen and hydrogen are impelled by pressure (transpiration) in the ratio of 1 to 2·3, instead of 1 to 4, the relation of diffusion. Hence the oxygen travels through the diaphragm, partly in one of these ratios and partly in the other, and the proportion of oxygen which enters the vessel is increased, as in Bunsen's experiments.‡

DEVELOPMENT OF HEAT BY CHEMICAL ACTION.

From the time when Lavoisier pointed out the true nature of the phenomenon of combustion, the measurement of the heat evolved in chemical combination has occupied a prominent place in the attention of chemists, and has been made the subject of numerous researches, the most exact and comprehensive of which, are those of Messrs. Favre and Silbermann, and of Dr. Andrews.§

The apparatus used by Favre and Silbermann for measuring the heat evolved by the combustion of various substances in oxygen gas, is represented, with the omission of minor details, in figure 232. *C* is a vessel of gilt brass plate, immersed in a water-calorimeter, *A A*, of silvered copper-plate, and the latter is enclosed in an outer vessel, *B B*, the space between *A* and *B* being filled with

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* See Bunsen's "Gasometry," translated by Dr. Roscoe, pp. 198—233.

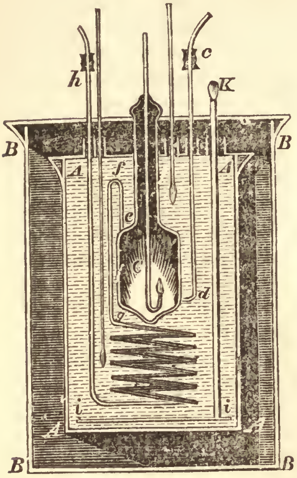
† Compare the figure at page 88 of this work, with figure 53, p. 202, of Bunsen's "Gasometry."

‡ Ann. Ch. Phys. [3], xxxiv. 357; xxxvi. 5; xxxvii. 405; Abstr. Chem. Soc. Qu. J. vi. 234.

§ Phil. Mag. [3], xxxii. 321, 392, and 426.

swan-down, to prevent the escape of heat from the water in *A*. The vessels *A* and *B* are closed with lids having apertures for the insertion of tubes and thermometers. The combustions are performed in the vessel *C*, into which oxygen gas is introduced through the tube *c d*, and the gaseous products of the combustion escape by the tube *e f g h*, the lower part of which is bent into numerous coils, to facilitate as much as possible, the transmission of the heat of these gases to the water in the calorimeter. The extremity *h*, of this tube is connected with a gasometer, or with an absorbing apparatus. To ensure uniformity of temperature in the water, a flat ring of metal *i i*, is moved up and down by means of the rod *K i*. Combustible gases were introduced into the vessel *C*, by means of fine tubes, the gas being previously set on fire at the aperture. Solid bodies were attached to fine platinum wires suspended from the lid of the calorimeter: liquids were burned in small capsules or in lamps with asbestos wicks; charcoal was disposed in a layer on a sieve-formed bottom, through the openings of which the oxygen had access to it. The heat evolved was measured by the rise of temperature of the known quantity of water in the calorimeter.

Fig. 232.



For processes which take place without access or escape of gases, simpler apparatus may be used. For such reactions Favre and Silbermann employed a *mercury-calorimeter* (fig. 233), consisting of a glass globe filled with mercury, and having inserted into it a tube *a*, to contain the combining substances, an acid and a base for instance. The mercury in the globe communicates by the bent tube *b*, with the capillary tube *c d*, on which its expansion is measured. The apparatus forms, in fact, a large mercurial thermometer.

Fig. 233.

The unit of weight to which the following numbers refer is the gramme, and the unit of heat is the quantity required to raise the temperature of 1 gramme of water from 0° to 1° C.

Substance.	Formula.	Products.	Heat of Combustion.		Observers.
			1 Grm. of Substance with Oxygen.	1 Grm. of Oxygen with Substance.	
GASES.					
Hydrogen	HH	$H_2\Theta$	34462	4308	F. S.
			33802	4226	A.
Carbonic oxide........	$\text{Ꞓ}\Theta$	$\text{Ꞓ}\Theta_2$	2403	4205	F. S.
			2431	4255	A.
Marsh-gas..............	$\text{Ꞓ}H_4$	$\text{Ꞓ}\Theta_2$ and $H_2\Theta$	13063	3266	F. S.
			13168	3277	A.
Olefiant-gas............	Ꞓ_2H_4	"	11858	3458	F. S.
			11942	3483	A.

Substance.	Formula.	Products.	Heat of Combustion.		Observers.
			1 Grm. of Substance with Oxygen.	1 Grm. of Oxygen with Substance.	
LIQUIDS.					
Amylene	$Ꞓ_5H_{10}$	“	11491	3352	F. S.
Oil of turpentine	$Ꞓ_{10}H_{16}$	“	10852	3294	“
Ether	$Ꞓ_4H_{10}Ɵ$	“	9028	3479	“
Wood-spirit	$ꞒH_4Ɵ$	“	5307	3538	“
Alcohol	$Ꞓ_2H_6Ɵ$	“	7184	3442	“
Amylic alcohol	$Ꞓ_5H_{12}Ɵ$	“	8959	3285	“
Acetic acid	$Ꞓ_2H_4Ɵ_2$	“	3505	3286	“
Butyric acid	$Ꞓ_4H_8Ɵ_2$	“	5647	3106	“
Valerianic acid	$Ꞓ_5H_{10}Ɵ_2$	“	6439	3158	“
Palmitic acid (solid)	$Ꞓ_{16}H_{32}Ɵ_2$	“	9316	3240	“
Stearic acid (solid)	$Ꞓ_{18}H_{36}Ɵ_2$	“	9716	3317	“
Formiate of methyl	$Ꞓ_2H_4Ɵ_2$	“	4197	3935	“
Acetate of methyl	$Ꞓ_3H_6Ɵ_2$	“	5342	3529	“
Formiate of ethyl	$Ꞓ_3H_6Ɵ_2$	“	5279	3488	“
Acetate of ethyl	$Ꞓ_4H_8Ɵ_2$	“	6293	3461	“
Butyrate of methyl	$Ꞓ_5H_{10}Ɵ_2$	“	6791	3334	“
Butyrate of ethyl	$Ꞓ_6H_{12}Ɵ_2$	“	7091	3213	“
Valerate of methyl	$Ꞓ_6H_{12}Ɵ_2$	“	7376	3342	“
Spermaceti (solid)	$Ꞓ_{32}H_{64}Ɵ_2$	“	10342	3301	“
Sulphide of carbon	$ꞒS_2$	$ꞒƟ_2$ and $SƟ_2$	3401	2692	“
SOLIDS.					
Carbon (wood charcoal	$Ꞓ$	$ꞒƟ$	2473	1855	F. S.
		$ꞒƟ_2$	8080	3030	“
Sulphur (rhombic)	S	$SƟ_2$	2221	2221	“
Phosphorus (yellow)	PP	$P_2Ɵ_5$	5953	4613	“
Zinc	ZnZn	$Zn_2Ɵ$	1301	5366	A.
Iron	FeFe	$Fe_3Ɵ_2$	1575	4134	“
Tin	SnSn	$SnƟ$	1167	4230	“
Protoxide of tin	$Sn_2Ɵ$	$SnƟ$	521	4349	“
Copper	CuCu	$Cu_2Ɵ$	604	2394	“
Red oxide of copper	$Cu_4Ɵ$	$Cu_2Ɵ$	256	2288	“

A comparison of the numbers in this Table, shows that the quantities of heat evolved by the combination of a constant weight of oxygen with different combustible bodies, are much more nearly equal than the quantities evolved by the combustion of equal weights of these several bodies. Nevertheless, the conclusion drawn from older experiments (p. 229), that the quantity of heat evolved in combustion is always proportionate to the quantity of oxygen consumed, is very far from being confirmed by the numbers in the fifth column of the preceding Table.

Equal weights of isomeric bodies do not evolve equal quantities of heat in combustion. This may be seen by comparing the numbers for formiate of ethyl and acetate of methyl, for acetic acid and formiate of methyl, &c.

In homologous organic compounds, the heat of combustion for equal weights of the compounds increases, as the carbon and hydrogen bear a greater proportion to the oxygen. This may be seen in the series of alcohols, fatty acids, and compound ethers.

In general, the heat evolved by the combustion of an oxidized body, such as carbonic oxide, or protoxide of tin, is less than that which is evolved in the complete oxidation of the combustible constituent.

But little is known respecting the relation which the heat of combustion of a compound of two or more combustible substances bears to the sum of the heats of combustion of its constituents. In some cases, it is less than that sum (*e. g.* marsh-gas and olefiant gas); in others, greater (bisulphide of carbon, oil of turpentine). The relation in question is, doubtless, greatly affected by the molecular states of the compound and of its elements in the separate state. That the heat of combustion of a body is materially influenced by its state of aggregation, is shown by many experiments; and in general it is found that, of two modifications of a substance, that which has the greater specific heat, likewise evolves the greater quantity of heat in combination. Thus, the specific heat of yellow phosphorus is greater than that of the red variety; now 1 gramme of yellow phosphorus, in burning to phosphoric acid, evolves 5953 heat-units, whereas the same quantity of red phosphorus evolves only 5070 heat-units. The same relation is strikingly shown by the following comparison of the quantities of heat evolved in the complete combustion of equal weights of different kinds of carbon, as determined by Favre and Silbermann, with their specific heats, as determined by Regnault: —

	Heat of Combustion.	Specific Heat.
Wood-charcoal	8080	0·24150
Coke from gas-retorts	8047	0·20360
Native graphite	7797	0·20187
Graphite from blast-furnaces	7762	0·19702
Diamond	7770	0·11687

Sulphur likewise evolves in combustion different quantities of heat, according to its state of aggregation. Octohedral sulphur, native or artificial, gives, as a mean result, 2221 heat-units; prismatic sulphur, recently crystallized from fusion, gives 2260 heat-units.

Combination of Metals with Chlorine, Bromine, and Iodine. — To determine the heat evolved in the combination of metals with chlorine, Andrews introduced the metals, enclosed in thin glass bulbs, into a glass vessel filled with dry chlorine. This vessel was placed within the water-calorimeter, and the glass bulb broken by shaking the vessel. The results are given in the following Table. The number for hydrogen is from the experiments of Favre and Silbermann :—

Substance.	Product.	Heat of Combustion.	
		1 Gramme of Substance with Chlorine.	1 Gramme of Chlorine with Substance.
Hydrogen	HCl	23783	670
Potassium	KCl	2655	2932
Zinc	ZnCl	1529	1404
Copper	CnCl	961	858
Iron	Fe_2Cl_3	1745	317
Tin	$SnCl_2$	1079	881
Arsenic	$AsCl_3$	994	700
Antimony	$SbCl_3$	707	799

If we multiply the numbers which express the heat of combination of 1 gramm of each of the metals with oxygen and chlorine, by the atomic weights of the several metals, we obtain the following numbers for the quantities of heat evolved by equivalent quantities of these metals in combining with oxygen and chlorine :—

			With 8 gr. Oxygen.	With 35·5 gr. Cl.
1	gramme of	hydrogen	34462	23783
32·6	"	zinc	42413	49844
31·7	"	copper	19147	30464
29	"	tin (to $Sn\Theta$ and $SnCl_2$)	33843	31291

The numbers in this Table do not exhibit any simple relation to each other, so that no conclusion can be drawn from them as to the quantity of heat evolved or absorbed in the substitution of chlorine for oxygen, or of one metal for another in combination with either of these elements. Here, as in other cases, the difference in the state of aggregation doubtless interferes with the constancy of action which might otherwise be observed. The amount of interference arising from this cause is much diminished when compounds are compared in the state of aqueous solution; and accordingly it is found that, when the quantities of heat evolved by the combination of different bases and acids (or metals and radicals), in the form of soluble salts, are compared, numbers are obtained which exhibit a tolerably near approach to regular progression.

The following Table exhibits the number of units of heat evolved by equivalent quantities of different bases in combining with various acids, as determined by Favre and Silbermann: —

Bases.		Acids.					
		Sulphuric.	Nitric.	Hydrochloric.	Hydrobromic.	Hydriodic.	Acetic.
Grm.							
47·2	Potash	16083	15510	15656	15510	15698	13978
31	Soda	15810	15283	15128	15159	15097	13600
26	Oxide of ammonium.	14690	13676	13536	......	......	12649
76·5	Baryta	......	15360	15306	......	......	13262
28	Lime	......	16943	16982	......	......	14675
20	Magnesia	14440	12840	13220	......	......	12270
35·6	Manganous oxide	12075	10850	11235	......	......	9982
40·6	Zinc-oxide	10455	8323	8307	......	......	7720
64	Cadmic oxide	10240	8116	8109	......	......	7546
39·7	Cupric oxide	7720	6400	6416	......	......	5264
37·6	Nickel-oxide	11932	10450	10412	......	......	9245
37·5	Cobaltous oxide	11780	9956	10374	......	......	9272
111·7	Lead-oxide	......	9240	......	......	......	7168
116·1	Silver-oxide	......	6206	......	......	......	......

A comparison of these numbers shows that nitric, hydrochloric, hydrobromic, and hydriodic acids, in combining with the same base, evolve nearly equal quantities of heat; sulphuric acid a considerably greater, and acetic acid a smaller quantity. Among the bases, the alkalies evolve the greatest quantity of heat in combining with any acid. In general, it appears that the greatest heat is evolved by the combination of the strongest acids with the strongest bases.

The corresponding terms of any two horizontal rows in the preceding table exhibit, in some cases, nearly equal differences; and the same is true with regard to the corresponding terms of any two vertical rows. If these differences were constantly equal, it would follow that the quantities of heat evolved or absorbed in the substitution of a base *a* for a base *b* (potash for soda, for example), would be the same with whatever acid the base were united; and, similarly, the heat evolved or absorbed in the substitution of one particular acid for another, would be independent of the bases. The actual differences, however, deviate too much from this law to warrant its reception as an expression of the results of observation. Nevertheless, there is a considerable degree of *à priori* probability in its favour; and the observed deviations from it may perhaps arise from disturbing causes, such as the different quantities of heat absorbed in the solution of salts, &c. How far this is the case, remains to be decided by further experiments.

Heat is likewise evolved in the combination of acids with water. The following are the quantities of heat developed, according to Favre and Silbermann, by mixing sulphuric acid, SO_4H, with various proportions of water.

			Heat-units.	Differences.
With the first	$\frac{1}{8}$	atom water	9·4	0·6
second	$\frac{1}{8}$	“	8·8	
first	$\frac{1}{4}$	“	18·8	1·6
second	$\frac{1}{4}$	“	17·2	
first	$\frac{1}{2}$	“	36·7	8·4
second	$\frac{1}{2}$	“	28·3	
	1	“	64·7	29·9
	2	“	94·6	17·4
	3	“	111·9	10·3
	4	“	122·2	8·5
	5	“	130·7	5·5
	6	“	136·2	4·4
	7	“	141·8	3·3
	8	“	145·1	3·4
	9	“	148·5	0·0
	10	“	148·4	0·0
	20	“	148·6	

These numbers show that the heat evolved by adding a given quantity of water to hydrated sulphuric acid, diminishes as the quantity of water already present is greater.

Heat evolved by the solution of gases in water.—When a gas dissolves in water, heat is evolved, partly in consequence of the chemical combination, and partly from the condensation of the gas to the liquid state. According to Favre and Silbermann:—

			Heat-units.
1 gramme of	hydrochloric acid gas	dissolved in water evolves	449·6
1 “	hydrobromic “	“ “	235·6
1 “	hydriodic “	“ “	147·7
1 “	sulphurous “	“ “	120·4
1 “	ammoniacal gas	“ “	514·3

The heat evolved varies, however, according to the quantity of water in which a given quantity of the gas dissolves.

Solution of salts, &c., in water.—The calorific effect produced by the solution of a solid in a liquid, depends upon several circumstances; viz. on the chemical affinity between the two, on the quantity of heat absorbed in the passage of the solid to the liquid state, on the quantity of the solvent, and on the temperature at which the solution takes place. The result is, in most cases, an absorption of heat or reduction of temperature; in some cases, however, as when the act of solution is preceded or accompanied by the formation of a definite hydrate, the effect may be reversed. The combination of anhydrous potash with water to form the hydrate KO.HO, is attended with a rise of temperature sufficient to produce incandescence; the hydrate KO.HO likewise evolves a considerable quantity of heat on dissolving in water, because it first combines with a definite proportion of water, forming the hydrate $KHO_2.4HO$; but the solution of this latter compound in water produces a considerable fall of temperature. Anhydrous chloride of calcium combines with water, forming the hydrate CaCl.6HO, the combination being attended with great evolution of heat; but the solution of the hydrate in water produces cold.

The absorption of heat accompanying the solution of salts is not wholly due to the liquefaction of the solid; for the heat thus absorbed in solution is sometimes greater, sometimes less than when the salt is liquefied by heat alone. Thus, in the fusion of 1 gramme of nitrate of potash, 49 heat-units are rendered latent; but when the same salt is dissolved in 20 parts of water, at 20° C., 80 heat-units are absorbed. The latent heat of fusion of crystallized chloride of calcium is 41 heat-units; but when this hydrated salt dissolves in 12 parts of water at 8° C., only 19 heat-units are absorbed. (C. Person.*)

The following results are extracted from Person's determinations of the influence of the temperature and quantity of the solvent on the quantity of heat absorbed: —

Name of Salt.	Quantity of Water.	Temperature.	Units of Heat absorbed.
Chloride of sodium ...... 1 gramme	7·28	17·1 C.	13·5
	7·28	10·3	14·9
	7·28	0·2	18·7
Nitrate of soda .... "	5	22·7	47·1
	20	22·8	55·7
Nitrate of potash......... "	10	23·8	76·7
	10	5·5	80·2
	20	5·7	86·4
	20	19·7	80·5

Hence it appears that when a given quantity of a salt is dissolved in the same quantity of water at different temperatures, the quantity of heat absorbed is greater as the initial temperature is lower; and at the same temperature, the quantity of heat absorbed increases with the quantity of the solvent. A fall of temperature is sometimes produced by merely diluting a solution with water. (Person).

COLD PRODUCED BY CHEMICAL DECOMPOSITION.

The separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination. The truth of this proposition has been established by Dr. Woods† and Mr. Joule,‡ by comparing the heat evolved in the electrolysis of water, with that which is developed in a thin metallic wire by a current of the same strength. The current was first made to pass through a vessel containing acidulated water, the quantity of gas evolved in a given time determined, and also the rise of temperature, the strength of the current being at the same time measured by the tangent-compass (p. 679). The electrolytic cell was then removed, and a thin platinum wire introduced between the poles, of such a length as to produce a resistance equal to that of the electrolyte. The quantity of heat evolved in this wire was then determined, and found to exceed that which was previously evolved in the electrolytic cell, by a quantity equal to that which would be evolved in the combination of the oxygen and hydrogen eliminated by the current in the previous experiment.

The same proposition is likewise established by many other chemical phenomena. When zinc dissolves in dilute sulphuric acid, the action may be supposed to consist of three stages, viz., the decomposition of water, the formation of oxide of zinc, and the combination of the oxide of zinc with sulphuric acid, forming $ZnO . SO_3$. Now:

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* Ann. Ch. Phys. [3], xxxiii. 448.

† Phil. Mag. [4], ii. 368.

‡ Phil. Mag. [4], iii. 481.

	Heat-units.
The heat evolved in the oxidation of 1 atom or 32·6 parts of zinc,	= 42413
The heat evolved in the combination of 1 atom or 40·6 parts oxide of zinc with sulphuric acid, in presence of a large quantity of water (p. 755)	= 10455
Sumt	= 52868
Deducting from this the heat evolved in the combination of 1 atom or 1 gramme of hydrogen with oxygen	= 34462
There remains for the heat evolved in the entire process	18406

which agrees very nearly with the quantity determined by direct experiment, viz. 18,514 heat-units.

Again, when metallic oxides are reduced by hydrogen, the heat evolved is not so great as when the same quantity of hydrogen combines with free oxygen, because it is diminished by the heat absorbed in the separation of the oxygen and the metal.

The reduction of oxide of iron by hydrogen takes place without much evolution of heat, because the heat evolved in the combination of 1 grm. of oxygen with hydrogen, viz. 4308 heat-units (p. 752), is not much greater than that which is evolved when the same quantity of oxygen combines with iron, viz. 4134 heat-units. But the reduction of oxide of copper is attended with a rise of temperature amounting to incandescence, because the heat evolved in the oxidation of hydrogen greatly exceeds that which is evolved in the oxidation of copper, which is only 2393 heat-units.

The absorption of heat in decomposition is also demonstrated by the fact that no alteration of temperature takes place in the double decomposition of salts, provided all the products remain in solution; in fact, the heat evolved in the combinations is exactly compensated by the cold produced by the decompositions which take place at the same time. But if a precipitate is formed, heat is evolved in consequence of the passage of the compound from the liquid to the solid state.

There are some phenomena which appear to contradict the assertion that heat is always absorbed in chemical decomposition. The decomposition of some of the oxides of chlorine, and of the chloride and iodide of nitrogen, is attended with evolution of heat. It has also been shown by Favre and Silbermann, that, in the combustion of charcoal in nitrous oxide, more heat is evolved than when charcoal burns in pure oxygen; and that the decomposition of peroxide of hydrogen by platinum is attended with considerable rise of temperature. These apparent anomalies may, however, be reconciled with the general law, if we admit that all chemical actions may be regarded as double decompositions (pp. 690, 691). Thus, in the last case, regarding peroxide of hydrogen as water *plus* oxygen, the decomposition may be represented by the equation:—

$$\mathrm{HO.O + HO.O = 2HO + OO.}$$

And it is possible that the heat evolved in the combination of oxygen with oxygen, may be greater than that which is absorbed in the separation of the oxygen from the water; and similarly in the other cases.

NON-METALLIC ELEMENTS.

OXYGEN AND HYDROGEN.

Extraction of Oxygen from Atmospheric air. — Boussingault has shown* that it is possible to obtain oxygen gas in considerable quantity from the air by the use of baryta, that substance absorbing oxygen from the air at a low red heat, and being converted into peroxide of barium, and the latter, when raised to a higher temperature, — or still more easily when exposed to a current of aqueous vapour, —giving up its second atom of oxygen in the free state. The apparatus used consists of a tube of porcelain or glazed earthenware, communicating at the one end, by means of smaller tubes provided with stopcocks, with an aspirator and a gas-holder, and at the other with the external air and also with a steam-boiler. The tube is filled with hydrate of baryta, — mixed with lime or magnesia to diminish its fusibility,—and heated to low redness, a current of air being at the same time drawn through the tube by the aspirator. The hydrate of baryta is thereby converted into peroxide of barium ; and when the oxidation has proceeded far enough, the current of air is suspended, a jet of steam sent through the tube, and at the same time the connection with the gas-holder is opened ; the peroxide of barium is then reconverted into hydrate of baryta, and the excess of oxygen passes into the gas-holder. The hydrate of baryta may now be reoxidized by a fresh current of air, the resulting peroxide again decomposed by vapour of water, — and this series of operations may be repeated any number of times. Boussingault's first experiments were made with anhydrous baryta, which likewise absorbs oxygen when heated to low redness in a current of air, and gives it up again at a bright red heat. It was found, however, that the baryta, after one or two repetitions of the process, lost in a great measure its power of absorbing oxygen. In fact, baryta, when really anhydrous, shows but little inclination to absorb oxygen ; it is only the hydrate that is readily converted into BaO_2. Now baryta, when prepared in the ordinary way, by calcining the nitrate, always contains a little water, which facilitates the absorption of the oxygen ; but after being heated two or three times in a current of dry air, it becomes really anhydrous, and is then no longer oxidized. The use of hydrate of baryta is therefore much more advantageous, both for the reason just stated, and likewise because the decomposition of the peroxide by vapour of water takes place at a much lower temperature than by simple ignition. The process in this form is adapted for use on the large scale.†

Ozone (p. 232). — The nature of ozone is still a matter of discussion. That it is a higher oxide of hydrogen was first suggested by Professor Williamson,‡ who passed ozoniferous oxygen, obtained by electrolysis, first over chloride of calcium to dry it, and then through a glass tube, in which it was either heated by a spirit-lamp or brought in contact with finely divided copper at a red heat. The ozone was thereby decomposed and deprived of its odour, and water was deposited. The

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* Compt. rend. xxxii. 261 ; Ann. Ch. Phys. [3], xxx. 5 ; Chem. Soc. Qu. J. v. 269.

† A patent for the preparation of oxygen in this manner, and its application in various chemical operations, has been taken out by Messrs. Swindells and Nicholson. (Chem. Gaz. 1855, 139).

‡ Ann. Ch. Pharm. liv. 127. This view was afterwards adopted by Schönbein (*Pogg. Ann.* lxvii. 78), but he has since abandoned it, inclining rather to regard ozone as an allotropic modification of oxygen (*Ann. Ch. Pharm.* lxxxii. 232 ; *J. pr. Chem.* liii. 65).

same view has been further supported by the more recent experiments of Baumert,* who has likewise analyzed the ozone quantitatively, and finds that it is a *teroxide of hydrogen*, HO_3. In Baumert's experiments, ozoniferous oxygen evolved at the positive pole from water acidulated with sulphuric and chromic acids (which mixture was found to yield the largest quantity of ozone, not, however, exceeding 1 milligramme of that substance to 3½ litres of oxygen) was passed, after thorough drying, into a glass tube lined with a film of anhydrous phosphoric acid. On heating the tube with a spirit-lamp, the phosphoric acid became transparent, and was dissolved at the part of the tube beyond the flame, showing that water was there deposited. It would appear then that ozone, obtained by electrolysis, contains the elements of water; and its powerful oxidizing properties show that it also contains an excess of oxygen. Hence, to analyze it quantitatively, it is only necessary to determine the proportion of this excess of oxygen in a known weight of ozone. The analysis was made by passing the ozoniferous oxygen, first through a tube containing pumice-stone soaked in sulphuric acid, to dry it; then through a bulb-apparatus containing solution of iodide of potassium, which completely absorbed the ozone, and was itself at the same time partially decomposed, a certain quantity of iodine being set free by the excess of oxygen in the ozone; and, lastly, through a second bulb-apparatus containing strong sulphuric acid, to absorb any water mechanically carried forward from the iodide of potassium solution by the stream of gas The increase of weight in the two bulb-apparatus gave the total quantity of ozone; and the quantity of iodine set free (estimated by Bunsen's volumetric method)† determined the amount of active oxygen therein. Two experiments made in this manner gave, in 100 parts of ozone:—$96·24\,O + 3·76\,H$, and $95·70\,O + 4·30\,H$ respectively. The formula, HO_3, requires $95·66\,O + 4·34\,H$. The oxidizing action of the ozone was found to be so powerful, that it quickly destroyed any organic substance, such as vulcanized caoutchouc, used to connect the different parts of the apparatus: hence it was necessary to make all the connections either by fusion or by grinding.

Baumert has also found, in accordance with the observations of previous experimenters, that perfectly dry oxygen gas, subjected for some time to the action of the electric spark, is brought into an allotropic state, in which its combining tendencies are highly exalted, so that is capable of overcoming the most powerful affinities, such as that of chlorine or iodine for potassium, at ordinary temperatures. Ozonized oxygen was freed from ozone and aqueous vapour by passing through sulphuric acid, through a heated glass tube, over fragments of iodide of potassium, and through pulverulent phosphoric acid, and then made to pass through a glass tube having platinum wires fixed into its sides. On passing a rapid succession of electric sparks between these wires, the gas acquired again the odour of ozone, and the power of decomposing a solution of iodide of potassium, characters which it did not possess before the sparks were passed through it. When heated to 200° C. it lost these peculiar properties, and was restored to its ordinary state. Results similar to this had previously been obtained by Marignac and De la Rive, and also by Fremy and Becquerel.‡ In the experiments of the last-mentioned philosophers, perfectly dry oxygen gas, enclosed in sealed glass tubes, and subjected to the continued action of electric sparks passed along the *outer* surface of the glass, was found to acquire the power of decomposing iodide of potassium, and was absorbed by moist mercury or silver, and by solution of iodide of potassium. From these experiments it may be reasonably concluded that oxygen can by certain means be brought into a modified and excited condition; but as this modified oxygen, when it exhibits the odour of ozone, or any of its peculiar reactions, is necessarily brought into contact with moisture, it is likewise high probable that it

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* Pogg. Ann. lxxxix. 38; Chem Soc. Qu. J. vi. 169.

† Ann. Ch. Pharm. lxxxvi. 265.

‡ Ann. Ch. Phys. [3], xxxv. 62; Chem. Soc. Qu. J. v. 272.

then combines with the elements of water, forming the true ozone HO_3, and that to this the odour and oxidizing actions are really due.

Ozone, formed by the slow oxidation of phosphorus in the air, exhibits the same characters as that which is obtained by electrolysis of water, &c. Ozone thus produced is generally regarded as merely allotropic oxygen; but as water is always present in in its formation, it may also be a peroxide of hydrogen, like the ozone obtained from electrical sources.*

According to Schönbein, many other substances besides phosphorus possess the power of inducing the formation of ozone. Thus, ether, oil of turpentine, oil of lemons, linseed oil, alcohol, wood-spirit, various vegetable acids, sulphuretted hydrogen, arseniuretted hydrogen, and sulphurous acid, in contact with air or oxygen gas, and under the influence of light, acquire the power of decolourizing indigo, and producing various oxidizing actions. A similar influence is exerted by mercury and other noble metals in the finely divided state; and stibethyl is found to be a more powerful ozonizer than even phosphorus itself.

Houzeau has shown† that active oxygen may be obtained by the action of strong (monohydrated) sulphuric acid on peroxide of barium. The gas thus evolved has a very powerful odour, and a taste like that of the lobster; it rapidly decolourizes blue litmus paper; oxidizes silver; burns ammonia spontaneously, transforming it into nitrate of ammonia; instantly burns phosphuretted hydrogen (the less inflammable variety, p. 326) with emission of light; decomposes hydrochloric acid, setting the chlorine free; is a powerful oxidizing and chlorinizing agent; is stable at ordinary temperatures, but loses its peculiar properties when heated to 75° C. In all these respects it differs essentially from ordinary oxygen; in fact it exhibits the properties of ozone. Active oxygen may also be obtained from other bodies besides the peroxide of barium. Oxygen in the combined state appears, indeed, to possess the intensified power which distinguishes free oxygen in the nascent state.

The nature of ozone has also been investigated by Dr. Andrews,‡ who has arrived at the conclusion that electrolytic ozone, as well as that obtained from other sources, is nothing but active oxygen. The excess of the weight of ozone in Baumert's experiments, over that of the active oxygen, is attributed by Andrews to the presence of a small quantity of carbonic acid, which he states is always mixed with the gases resulting from the decomposition of water, unless especial precautions be taken to get rid of it, and being absorbed by the potash resulting from the decomposition of the neutral solution of iodide of potassium, increases the weight of the apparatus, and consequently produces an apparent increase in the quantity of ozone absorbed.

To obviate this supposed source of inaccuracy, Andrews, using an apparatus similar to that of Baumert, acidulated his solution of iodide of potassium with hydrochloric acid; and, in five experiments, in which 29 litres of the ozoniferous gas were passed through the apparatus, obtained an increase of weight in the absorption-bulbs, that is to say, a quantity of ozone — amounting to 0·1179 grm., while the quantity of active oxygen, estimated according to the quantity of iodine separated, was 0·1178 grm. From this result, Andrews concludes that ozone is nothing but an active form of oxygen.

In another series of experiments, in which electrolytic ozone was decomposed by heat, and the gas subsequently passed over strong oil of vitriol and anhydrous phosphoric acid, not a trace of water could be discovered. Andrews has likewise confirmed the result obtained by other experimenters that pure dry oxygen acquires peculiar active properties by the action of the electric spark; and by comparing the properties of ozone obtained from various sources, he concludes that

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* Williamson, Ann. Ch. Pharm. lxi. 32.

† Compt. rend. xl. 947.

‡ Chem. Soc. Qu. J. ix. 168.

ozone, in whatever manner produced, is essentially the same, consisting in fact of allotropic oxygen.

On the other hand, Baumert* denies the existence of carbonic acid in the ozoniferous gas which he obtained by electrolysis, inasmuch as the electrolyte used, water acidulated with sulphuric and chromic acid, could scarcely absorb a sufficient quantity of carbonic acid to account for the results obtained. He moreover attributes the carbonic acid which Andrews obtained, to the oxidizing action of the ozone on the diaphragm of bladder with which the positive cell of the decomposing apparatus was closed. Baumert finds, indeed, that when a diaphragm of bladder is used for this purpose, carbonic acid is actually produced; but when a diaphragm of gypsum is employed, not a trace of that gas can be detected. With respect to the use of iodide of potassium acidulated with hydrochloric acid, Baumert calls attention to the fact that such a solution must contain free hydriodic acid, which is decomposed by oxygen in its ordinary as well as in its allotropic state. In fact, oxygen gas evolved by electrolysis, and completely freed from ozone by passing through a neutral solution of iodide of potassium, liberated, when subsequently passed through a solution of the same salt acidulated with hydrochloric acid, a quantity of iodine much larger than that which it had previously separated from the neutral solution. This may account for the greater proportion of the active oxygen to the total quantity of ozone obtained in the experiments of Andrews.

The true nature of ozone must then still be considered a matter for investigation. The existence of an allotropic modification of oxygen possessing peculiarly active properties appears to be established by the researches of numerous inquirers; but on the other hand, till some more valid objection is adduced against the results obtained by Baumert and Williamson, the existence of hydrogen in the ozone obtained by electrolysis of acidulated water can scarcely be denied.

Quantitative estimation of Oxygen and Hydrogen.—The quantity of either of these gases in a gaseous mixture may be determined by mixing it with an excess of the other, and inducing combination by the electric spark, or by spongy platinum or platinized charcoal. One-third of the volume of gas which disappears is oxygen, and two-thirds hydrogen. This, of course, implies that no other gases are present capable of uniting with either oxygen or hydrogen.

The amount of hydrogen in solid or liquid compounds (generally organic), when it is not present in the form of water, is estimated by heating the compound in contact with some oxidizing agent, generally oxide of copper, and weighing the water produced (p. 771). Oxygen in such compounds is generally determined by loss, the quantities of all the other elements being determined by the methods severally applicable to them, and the remainder being estimated as oxygen. The quantity of oxygen in metallic oxides which are not reduced by heat alone, is generally estimated by igniting them in a current of hydrogen and weighing the water produced.

The quantity of oxygen in the atmosphere may be determined by methods already described (p. 249). A very good method has since been given by Liebig,† viz., to absorb the oxygen by means of an alkaline solution of pyrogallate of potash. Pyrogallic acid is readily obtained as a crystalline sublimate by the dry distillation of gallic acid; it dissolves easily in potash: and the solution introduced by means of a pipette into air standing over mercury, absorbs the oxygen quickly and completely.

Estimation of Water.—The quantity of water in a solid compound, a salt for example, is determined by heating a weighed quantity of the substance in a capsule or crucible over a lamp, or in a sand-bath, or over a water-bath, according to

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* Pogg. Ann. xcix. 88.

† Chem. Soc. Qu. J. iv. 221.

the temperature which it will bear without giving off anything but water. Substances which will not bear even the temperature of the water-bath, are dehydrated by placing them over strong sulphuric acid, sometimes in vacuo, sometimes by merely placing the dish containing the sulphuric acid, with the substance supported above it in a capsule, on a ground glass plate, and covering the whole with a bell jar. Another method of drying substances which will not bear much heat, is to place them in a bent tube immersed in a water-bath at a regulated temperature, and pass through the tube a current of dry air, hydrogen, or carbonic acid, according to the nature of the substance.

Some salts when heated give off a portion of their acid as well as their water, the sulphates of alumina, and sesquioxide of iron for example. To determine the quantity of water in such cases, the salt must be mixed with a weighed quantity of protoxide of lead, sufficient to cover it completely, and heated in a platinum crucible: the acid, which would otherwise escape, is then retained by the oxide of lead, and nothing but water goes off.

The quantity of combined water in a base, such as hydrate of potash, is determined by heating the base with an acid which will form with it a compound not decomposable at a red heat.

In all cases, the water, instead of being estimated merely by loss of weight, may be determined by receiving it in a tube filled with dry chloride of calcium, or with pumice stone soaked in strong sulphuric acid, an empty glass bulb, previously weighed, being, however, interposed when the quantity of water is large (p. 238, fig. 108). This method is particularly applicable when other substances besides water are given off at the same time.

The methods of determining the quantity of water in solutions are similar to those above described for solids (p. 385).

Absorption of gases by water and other liquids.—The laws relating to the absorption of gases by liquids have lately been examined with great care by Bunsen, whose results tend partly to confirm, partly to modify those of the older experiments of Dalton, Henry, and Saussure (p. 81, 240).

The absorption of the more soluble gases, such as ammonia, sulphurous acid, &c., was estimated by saturating the liquid with the gas at a known temperature, and then determining, either by volumetric, or by weighed analyses, the quantity of gas dissolved in a given volume of the liquid; for example, hydrosulphuric acid was precipitated by a solution of copper, sulphurous acid and chlorine were determined by the iodometric method, to be afterwards described.

For the less soluble gases, a different method was adopted. The apparatus used for the purpose, called an *absorptiometer*, consists of a graduated tube closed at the top, and containing mercury. The gas is first introduced into this tube above the mercury, and afterwards the absorbing liquid. This tube is enclosed within a wider one, the space between the two being filled with water, by means of which any required temperature may be imparted to the contents of the inner tube. The outer tube is closed at top with a lid, in the middle of which is an elastic cushion pressing firmly on the inner tube containing the gas. This tube, by a peculiar contrivance, may be either firmly closed at the bottom, or made to communicate with the mercury in the cistern in which it stands. The tubes being filled and firmly closed top and bottom, the whole is vigorously shaken for about a minute, to bring the gas well in contact with the liquid. The inner tube is then loosened at the bottom, so as to open a communication with the mercury in the cistern, and equalize the pressure. More gas is then introduced, and the shaking repeated, and these operations are continued, till the mercury in the inner tube no longer exhibits any alteration of level. The volume of the remaining gas is then read off, and observations made of the pressure and temperature.

The volume of a gas, reduced to 0° C., and 760 mm. pressure, which is absorbed by the unit of volume of any liquid, is called the *coefficient of absorption*.

The formula used by Bunsen for calculating these coefficients is founded on the law of gas-absorption discovered by Dr. Henry, viz. that at any given temperature, the weight of a gas absorbed by a given quantity of a liquid is proportional to the pressure; or, in other words, that the volume of the gas absorbed at any given temperature is the same under all pressures (p. 81). Bunsen finds, indeed, that the coefficient of absorption of any gas thus determined under different pressures, exhibits a constant value, a result which affords a striking confirmation of the truth of Henry's law.

If V and V' denote the volumes of a gas reduced to 0°, before and after absorption, P and P' the corresponding pressures, the quantity of gas absorbed under the pressure P' is $\frac{VP}{0{\cdot}760}-\frac{V'P'}{0{\cdot}760}$. To reduce this to the normal presssure, 0·760 mm., it must be multiplied by $\frac{0{\cdot}760}{P'}$; and if the volume of the absorbing liquid is h, the coefficient of absorption α, or the quantity of gas absorbed by a unit volume of the liquid, will be

$$\alpha = \frac{1}{h}\left\{\frac{VP}{P'} - V'\right\}.$$

The following table exhibits the coefficients of absorption of certain gases by water and alcohol for every 5 degrees centigrade of temperature:—

	Oxygen.		Hydrogen.		Nitrogen.		Nitrous Oxide.	
	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.
0° C.	0·04114	0·28397	0·0193	0·06925	0·02035	0·12634	1·3052	4·1780
5	0·03628			0·06853	0·01794	0·12440	1·0954	3·8442
10	0·03250			0·06786	0·01607	0·12276	0·9196	3·5408
15	0·02989			0·06725	0·01478	0·12142	0·7778	3·2678
20	0·02838			0·06668	0·01403	0·12038	0·6700	3·0253
25	?			0·06616	....	0·11964	0·5962	2·8133

	Carbonic Oxide.		Carbonic acid.		Marsh Gas.		Olefiant Gas.	
	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.
0° C.	0·03287	0·20443	1·7967	4·3295	0·05449	0·52259	0·2563	3·5950
5	0·02920		1·4497	3·8908	0·04885	0·50861	0·2153	3·3234
10	0·02635		1·1847	3·5140	0·04372	0·49535	0·1837	3·0859
15	0·02432		1·0020	3·1993	0·03909	0·48280	0·1615	2·8825
20	0·02312		0·9014	2·9465	0·03499	0·47096	0·1488	2·7131
25	....		....	2·7558	....	0·45982	....	2·5778

	Sulphurous Acid.		Hydrosulphuric Acid.		Chlorine.	Nitric Oxide.	Ammonia.
	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.
0° C.	79·789	327·80	4·3706	17·891	....	0·31606	1049·60
5	67·485	251·24	3·9652	14·766	....	0·29985	917·90
10	56·647	190·02	3·5858	11·992	2·5852	0·28609	812·76
15	47·276	144·13	3·2326	9·539	2·3681	0·27478	727·22
20	39·374	113·56	2·9053	7·415	2·1565	0·26592	653·99
25	32·786	98·33	2·6041	5·623	1·9504	0·25951	585·94
30	27·161	....	2·3290	....	1·7499		
35	22·489	....	2·0790	....	1·5550		
40	18·766	....	1·8569	....	1·3655		

When a liquid is in contact with a mixture of several gases, with none of which it is disposed to form a definite compound, it absorbs of each gas a quantity corresponding to the pressure which this same gas exerts in the mixture that remains after the absorption is complete. Now, in any mixture of gases, each gas exerts the same pressure that it would if it alone filled the entire space; and the pressure of the entire mixture is equal to the sum of the pressures of the separate constituents. If, for example, atmospheric air, which in 100 volumes contains 20·9 vols. oxygen, and 79·1 vols. nitrogen, exerts altogether a pressure equal to that of 760 mm. of mercury, the pressure of the oxygen is equal to $\frac{20 \cdot 9}{100} . 760 =$ 158·8 mm. and that of the nitrogen is $\frac{79 \cdot 1}{100} . 760 = 601 \cdot 2$ mm.

When water is saturated with atmospheric air, it takes up of each constituent a quantity determined by the existing temperature, and the partial pressure of each gas. For example, at 13° C., and under a pressure corresponding to 760 mm. of mercury, 1 volume of water absorbs $0 \cdot 03093 \times \frac{158 \cdot 8}{760} = 00646$ vols. of oxygen, measured at 0° C. and 760 mm.; and $0 \cdot 01530 \times \frac{601 \cdot 2}{760} = 0 \cdot 01210$ vols. nitrogen, also measured at the standard pressure and temperature. Hence, at 13° C. and 760 mm., 1 vol. water absorbs 0·00646 vols. oxygen, and 0·01210 vols. nitrogen, making together 0·01856 vols. of a gaseous mixture, containing 34·8 vols. oxygen, and 65·2 vols. nitrogen. Direct analysis of a gaseous mixture evolved by boiling, from water previously saturated with atmospheric air, gave 34·73 vols. pure oxygen and 65.27 vols. nitrogen.

When water previously saturated with oxygen or nitrogen is exposed to the air, the final result is still the same, the excess of either gas being given off, and the oxygen and nitrogen being ultimately absorbed in the proportions just given. If water containing any other gas is exposed to the air, the whole of the dissolved gas is ultimately eliminated, and the water becomes saturated with the atmospheric gases, in the same proportion as if no other gas had been previously dissolved in it. An exception, however, occurs when the dissolved gas is capable of forming a definite compound with the water, in which case portions of the gas and the water evaporate together.

The general law above stated with regard to the absorption of gaseous mixtures is found to hold good in mixtures of sulphurous acid gas with hydrogen and carbonic acid; of carbonic oxide and carbonic acid; and of carbonic oxide, marsh-gas, and hydrogen; but not with a mixture of equal volumes of chlorine and hydrogen, or of chlorine with twice or four times its volume of carbonic acid.

NITROGEN.

Preparation of Nitrogen gas (p. 244).—This gas may be obtained in great abundance, and perfectly pure, by heating a solution of nitride of potash with sal-ammoniac:—

$$KO.NO_3 + NH_4Cl = KCl + 4HO + 2N.$$

The solution of nitrite of potash is prepared by passing the nitrous gas, evolved by heating 1 part of starch with 10 parts of nitric acid, into a solution of caustic potash of sp. gr. 1·38, till the liquid becomes decidedly acid, and then adding a sufficient quantity of caustic potash to restore the alkaline reaction. The solution of nitrite of potash thus obtained may be preserved without alteration. On mixing this liquid with three times its bulk of concentrated solution of sal-ammoniac, and heating the mixture in a flask, nitrogen gas is given off in large quantity and with perfect regularity. Pure nitrogen may also be obtained by heating a solution of nitrite of ammonia; but this salt is difficult to prepare (Corenwinder.*)

Another method of obtaining nitrogen, mixed however with chlorine, is to heat a mixture of nitrate of ammonia and sal-ammoniac:—

$$2(NH_4.NO_6) + NH_4Cl = 5N + Cl + 12HO.$$

After the mixture has been heated to the melting point of the nitrate, the reaction goes on by itself. The chlorine may be afterwards absorbed by potash. (Maumené.†)

Nitrous oxide (p. 255).—This gas may be obtained in a state of purity by the action of protochloride of tin on aqua-regia. The tin-salt is dissolved in hydrochloric acid, the solution heated over the water-bath, and crystals or cylindrical lumps of nitre, successively dropped into it through a wide tube dipping into the liquid. (Gay-Lussac.‡)

Nitric oxide may be obtained by a process similar to that above described for the preparation of nitrous oxide, using however protochloride of iron instead of protochloride of tin. (Pelouze and Gay-Lussac.§)

Anhydrous nitric acid, NO_5, is obtained by the action of dry chlorine on nitrate of silver. Chlorine gas contained in a gasometer standing in sulphuric acid, is made to pass very slowly, first over chloride of calcium, then over sulphuric acid, and lastly over thoroughly dried nitrate of silver, which is heated, first to 95° C., and afterwards constantly to 58° or 60° C. The products of decomposition pass into a U-tube cooled to 21° C., in which a very volatile liquid (probably nitrous acid) collects, together with crystals of anydrous nitric acid, while oxygen escapes. The different parts of the apparatus must be connected by fusion, as the acid vapours would quickly corrode caoutchouc joints. The anhydrous nitric acid crystallizes in colourless rhombic prisms, having angles of about 60° and 120°, and in hexagonal prisms derived therefrom. It melts at 29° to 30° C., and boils at 45° to 50° C., but begins to decompose near its boiling point. It becomes strongly heated by contact with water, in which it dissolves without colouring or evolution of gas, forming hydrated nitric acid (H. Deville.‖) According to Dumas,¶ the crystals melt spontaneously when left to themselves; and on one occasion, when an attempt was made to recrystallize the fused mass by immersion in a freezing mixture, the tube was shattered with explosion.

Quantitative estimation of Nitrogen.—Nitrogen is estimated, either by collecting it as a gas in the free state and measuring its volume, or by converting it into ammonia. Most nitrogen-compounds, when strongly heated with the hydrates of the fixed alkalies, give off the whole of their nitrogen in the form of ammonia. This reaction is especially applied to the estimation of nitrogen in organic compounds, in which that element is united with carbon, hydrogen, &c. The organic compound is mixed with a large excess of soda-lime — a mixture of caustic soda and quick-lime, the latter being added to counteract the deliquescence of the hydrate of soda,—and heated to redness in a combustion-tube (p. 277), to which is attached a suitable bulb-apparatus containing hydrochloric acid. The ammonia is thereby absorbed, and is subsequently precipitated by chloride of platinum, in the manner described at page 619 of this volume. This method gives very exact results; but it is not applicable to compounds containing nitrogen in the form of nitric acid or of peroxide of nitrogen, because in such compounds the conversion

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* Ann. Ch. Phys. [3], xxvi. 296.

† Compt. rend. xxxiii. 401.

‡ Ann. Ch. Phys. [3], xxiii. 229.

§ Ann. Ch. Phys. [3], 216.

‖ Ann. Ch. Phys. [3], xxviii. 241.

¶ Compt. rend. xxviii. 323.

of the nitrogen into ammonia by heating with caustic alkalies is never complete. For such compounds, it is better to evolve the nitrogen in the free state, and determine its quantity by measurement. This may be done either comparatively or absolutely.

For the *comparative* determination, the azotized organic compound is mixed with oxide of copper, and heated in a combustion-tube, the open end of which, to the depth of four or five inches, is filled with finely-divided metallic copper, obtained by reducing the oxide with hydrogen. By the oxidizing action of the oxide of copper, the carbon of the organic compound is converted into carbonic acid, and the nitrogen into nitric oxide and other oxides of nitrogen, all of which are, however, completely decomposed in passing over the red-hot metallic copper, so that nothing but nitrogen and carbonic acid pass out. These gases are collected over mercury in a graduated tube, and their volume measured. The carbonic acid is then absorbed by potash, and the residual nitrogen also measured. Now the weights of equal volumes of nitrogen and carbonic acid are to one another as 14 to 22 (p. 130), that is to say, as the atomic weights of N and CO_2; and each atom of carbonic acid contains one atom of carbon. Consequently, the volumes of nitrogen and carbonic acid produced by the combustion of the organic compound, are to one another as the numbers of atoms of nitrogen and carbon. This method, of course, implies that the carbon in the organic compound has been previously determined.

For the *absolute* determination of nitrogen, the same method of combustion and collecting the gas is adopted, excepting that a longer combustion-tube is used, and a quantity of bicarbonate of soda is placed at the sealed end, sufficient to occupy about eight inches of the tube. The process is commenced by heating a portion of this bicarbonate of soda, so as to evolve carbonic acid, and sweep all the air out of the tube. The substance is then burned, and the evolved gases collected over mercury, the carbonic acid being absorbed by strong potash-ley placed at the top of the mercury; and when the combustion is ended, the remainder of the bicarbonate of soda is heated so as to evolve more carbonic acid, and drive all the remaining gases out of the tube. The volume of nitrogen collected is then read off and its weight calculated, the proper corrections being made for pressure and temperature. Dr. M. Simpson, of Dublin, has proposed certain modifications both in this and in the comparative method of estimating nitrogen, with the view of facilitating the process and insuring greater accuracy. The principal of these attentions is the replacement of the oxide of copper by oxide of mercury, which gives up its oxygen more readily, and, therefore, insures a more complete combustion, especially when the substance is rich in carbon.*

The method of combustion with oxide of copper and decomposition of the oxides of nitrogen by metallic copper, is applicable to all nitrogen compounds whatsoever. For the analysis of *nitrates*, in which the nitrogen is already completely oxidized, the oxide of copper may be dispensed with, the salt being simply ignited in a tube, and the nitrous vapours passed over red-hot metallic copper. *Nitric acid* may also be determined by several other methods. When it exists in the free state in aqueous solution, its quantity may be determined by shaking up the liquid with carbonate of baryta, till the nitric acid is completely neutralized, then filtering, evaporating the filter to dryness, care being taken not to heat the residue too strongly, and weighing the dry nitrate of baryta thus obtained. Or the solution of nitrate of baryta may be decomposed by sulphuric acid, the sulphate of baryta weighed, and the equivalent quantity of nitric acid calculated therefrom. If the solution of nitric acid is very weak, it is better to use baryta-water to neutralize it; then pass carbonic acid gas through the liquid to remove any excess of baryta; filter; and treat the filtered solution of nitrate of baryta as above.

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* Chem. Soc. Qu. J. vi. 289

When nitric acid is combined with a base, it may be liberated by distillation with sulphuric acid (p. 260), and the distillate treated with carbonate of baryta or baryta-water, in the manner already described. Or a weighed portion of the nitrate may be decomposed by sulphuric acid in a platinum crucible, the residual sulphate ignited and weighed, and the quantity of nitric acid thence determined by calculation. This method, however, is applicable only when the sulphate thus formed can bear a red-heat without decomposition.

For the estimation of small quantities of nitric acid, such as exist in plants, soils, and waters, some very ingenious methods have been invented by M. G. Ville.* The nitric acid is first converted into binoxide of nitrogen by boiling the solution of the nitrate with protochloride of iron and free hydrochloric acid:

$$NO_5 + 6FeCl + 3HCl = NO_2 + 3Fe_2Cl_3 + 3HO;$$

and the nitric oxide then converted into ammonia, either by passing it, mixed with excess of hydrogen, over spongy platinum heated nearly to redness;

$$NO_2 + 5H = NH_3 + 2HO;$$

or by passing it, mixed with excess of hydrogen and hydrosulphuric acid, over soda-lime heated nearly to redness:

$$NO_2 + 3HS + 2CaO = NH_3 + CaO.SO_3 + CaS_2.$$

The second method is generally the more exact of the two, the first giving accurate results only when the quantity of nitrogen to be determined is very small. The ammonia is absorbed by an acid of known strength contained in a bulb-apparatus, and its quantity determined by the alkalimetric method (p. 386); or it may be absorbed by hydrochloric acid, and precipitated by chloride of platinum. Another method is to pass the nitric oxide over red-hot metallic copper; but this method is not so exact as the preceding. To apply these methods to the determination of the quantity of nitrates in vegetable substances, soils, waters, &c., the substance (10 to 100 grammes) is exhausted with boiling water, and the concentrated solution treated as above.

Professor Way has also devised a method of estimating small quantities of nitric acid, especially adapted to rain-water and other waters. This process, which is a modification of Bunsen's volumetric method, consists in heating the solid residue obtained by evaporating about a pint of the water — previously rendered alkaline by lime-water to prevent loss of nitric acid—with hydrochloric acid and iodide of silver, in an apparatus from which the air has been completely excluded by a stream of carbonic acid gas, and exhaustion with the air-pump. The nitrates and the hydrochloric acid then decompose each other, with separation of nitric oxide and chlorine; and the chlorine decomposes the iodide of silver, liberating iodine, the amount of which is afterwards determined by a standard solution of sulphurous acid in the manner to be hereafter described. Organic matter, if present in the water, must be destroyed by adding a small quantity of permanganate of potash, during the concentration of the liquid.

The determination of the quantity of nitric acid in *nitrate of potash* is a process of considerable commercial importance, and several methods have been devised for it. Of these, however, there are only two in general use. The first, originally introduced by Gossart and improved by Pelouze, consists in boiling the acidified solution of the nitre with a solution of protochloride of iron of known strength, whereby the protoxide of iron is converted into sesquioxide, and binoxide of nitrogen is evolved, and afterwards determining the unoxidized portion of the iron by the method of Margueritte, with a standard solution of permanganate of potash (p. 458). According to Messrs. Abel and Bloxam,† this method does not always give exact results, because a portion of the nitre does not contribute to the oxidizing action, either from not being completely decomposed, or from losing a portion

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* Ann. Ch. Phys. [3], vi. 20.

† Chem. Soc. Qu. J. ix. 97; x. 107.

of its acid before it comes in contact with the iron-salt. The other method, introduced by Gay-Lussac, consists in deflagrating the nitre with one-fourth of its weight of finely divided charcoal (lamp-black) and 6 parts of common salt, the latter being added merely to moderate the action. The nitrate of potash is then converted into carbonate, the quantity of which in the ignited residue may be determined by the process of alkalimetry (p. 260). This method is also variable in its results, partly because a portion of the nitre is apt to escape decomposition, partly because cyanate of potash is formed during the reaction, and, when subsequently dissolved in water, is decomposed, with formation of carbonate of ammonia and carbonate of potash:

$$C_2NKO_2 + 4HO = KO.CO_2 + NH_4O.CO_2.$$

Hence, the quantity of alkali to be neutralized by the acid is greater than it should be. The presence of alkaline sulphates in the nitre also introduces an error, because these salts are reduced by ignition with charcoal to sulphides, which have an alkaline reaction. Messrs. Abel and Bloxam find that these several sources of error may be eliminated, and exact results obtained, by using the charcoal in a very finely divided state, and subsequently heating the ignited mass with chlorate of potash, which completely decomposes the cyanates and reconverts the sulphides into sulphates. The best form of carbon for the purpose was found to be the pure finely divided graphite prepared by Mr. Brodie's process (p. 770).

CARBON.

Volatility of carbon.—According to Despretz, charcoal exposed in vacuo to the heat produced by a Bunsen's battery of 500 or 600 pairs, disposed in 5 or 6 series, so as to form 100 pairs of 5 or 6 times the ordinary size, is volatilized, and collects on the sides of the vessel in the form of a black crystalline powder; in a space filled with a gas with which the carbon does not combine, volatilization likewise takes place, but more slowly. At the same temperature, charcoal may also be bent, welded, and fused, every kind of charcoal when thus treated becoming softer the longer the heat is continued, and being ultimately converted into graphite. Diamond exposed to the same temperature is likewise converted into graphite.*

Charcoal as a disinfectant.—The power which wood-charcoal possesses of absorbing and decomposing gaseous bodies has lately been applied by Dr. Stenhouse to the construction of ventilators and respirators for purifying infected atmospheres. In a pamphlet, bearing the title "On Charcoal as a Disinfectant," Dr. Stenhouse observes—"Charcoal not only absorbs effluvia and gaseous bodies, but, especially, when in contact with atmospheric air, rapidly oxidizes and destroys many of the easily alterable ones, by resolving them into the simplest combinations they are capable of forming, which are chiefly water and and carbonic acid. . . . . effluvia and miasmata are generally regarded as highly organized, nitrogenous, easily alterable bodies. When these are absorbed by charcoal, they come in contact with highly condensed oxygen gas, which exists within the pores of all charcoal which has been exposed to the air, even for a few minutes; in this way they are oxidized and destroyed." On this principle, Dr. Stenhouse has constructed *ventilators*, consisting of a layer of charcoal enclosed between two sheets of wire gauze, to purify the foul air which accumulates in water-closets, the wards of hospitals, and in the back courts and lanes of large cities. By the use of these ventilators, pure air may be obtained from exceedingly impure sources, the impurities being absorbed and retained by the charcoal, while a current of pure air alone is admitted into the neighbouring apartments. A similar contrivance might also be applied to the gully-holes of our common sewers, and to the sinks in private houses. Dr. Stenhouse has also constructed *respirators*, consisting of a

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* Compt. rend. xxviii. 755.

layer of charcoal a quarter of an inch thick, interposed between two sheets of silvered wire gauze, covered with woollen cloth. They are made either to cover the mouth and nose, or the mouth alone; the former kind of respirator affords an effectual protection against malaria and the deleterious gases which accumulate in chemical works, common sewers, &c. The latter will answer the same purpose when the atmosphere is not very impure, provided the simple precaution be taken of inspiring the air by the mouth, and expiring by the nose. This form of respirator may also be useful to persons affected with fetid breath. Freshly heated wood-charcoal simply placed in a thin layer in trays, and disposed about infected apartments, such as the wards of hospitals, is also highly efficacious in absorbing the noxious matter.

Platinized charcoal.—The power of charcoal in inducing chemical combination is greatly increased by combination with minutely divided platinum. In this manner, a combination may be produced possessing the absorbent power of charcoal (which is much greater than that of spongy platinum), and nearly equal, as a promoter of chemical combination, to spongy platinum itself. In order to platinize charcoal, nothing more is necessary than to boil it, either in coarse powder or in large pieces, in a solution of bichloride of platinum, and, when thoroughly impregnated, which seldom requires more than ten minutes or a quarter of an hour, to heat it to redness in a close vessel, a capacious platinum crucible being well adapted for the purpose. Charcoal thus platinized, and containg 3 grains of platinum in 50 grains of charcoal, causes oxygen and hydrogen gases to unite completely in a few minutes; with a larger proportion of platinum, the gases combine with explosive violence, just as if platinum-black were used. Cold platinized charcoal, held in a jet of hydrogen, speedily becomes incandescent, and inflames the gas. Platinized charcoal, slightly warmed, rapidly becomes incandescent in a current of coal gas; but does not inflame the gas, owing to the very high temperature required for that purpose. In the vapour of alcohol, or wood-spirit, platinized charcoal becomes red-hot, and continues so till the supply of vapour is exhausted. Spirit of wine, in contact with platinized charcoal and air, is converted in a few hours into vinegar. Two per cent. of platinum is sufficient to platinize charcoal for most purposes. Charcoal containing this amount of platinum causes oxygen and hydrogen to combine perfectly in about a quarter of an hour, and such is the strength of platinized charcoal which seems best adapted for disinfectant respirators. Charcoal containing only one per cent. of platinum causes oxygen and hydrogen to combine in about two hours; and charcoal containing the extremely small amount of $\frac{1}{4}$ per cent. of platinum produces the same effect in six or eight hours. Platinized charcoal seems likely to admit of various useful applications; one of the most obvious of these is its excellent adaptability to air-filters and respirators. From its powerful oxidizing properties, it may also prove a highly useful application to malignant ulcers and similar sores, on which it will act as a mild but effective caustic. It will probably also be found very useful in Bunsen's carbon battery (Stenhouse).*

Graphite.—This substance may be obtained in the pure and finely divided state by mixing it in coarse powder with $\frac{1}{14}$th of its weight of chlorate of potash, adding the mixture to a quantity of strong sulphuric acid equal to twice the weight of the graphite; heating the mixture in the water-bath as long as vapours of peroxide of chlorine are emitted; washing the cooled mass with water, and igniting the dry residue: it then swells up and leaves finely-divided graphite. A chemical compound of sulphuric acid with a peculiar oxide of carbon appears to be formed during the process. If the graphite to be purified contains silicious matters, a small quantity of fluoride of sodium must be added to the mixture before heating (Brodie†).

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* Chem. Soc. Qu. J. viii. 105.

† Ann. Ch. Phys. [3], xlv. 351.

Carbonic oxide. — This gas is rapidly absorbed by a solution of subchloride of copper in hydrochloric acid or ammonia, and indeed by the ammoniacal solutions of cuprous salts in general, *e. g.*, the sulphite. A definite compound is probably formed, containing copper and carbonic oxide in equal numbers of atoms, but no such compound has yet been isolated. Ferrous and stannous salts have no action on carbonic oxide (Leblanc[*]).

Preparation of olefiant gas (p. 285).—The frothing which causes so much inconvenience in the preparation of this gas by the action of sulphuric acid upon alcohol, may be completely prevented by adding a sufficient quantity of sand to convert the mixture into a thick, scarcely fluid mass. The decomposition may then be carried to the end without any frothing, and nearly all the carbon of the alcohol is obtained in the form of olefiant gas. Fifty grammes of alcohol of the strength of 80 per cent. yield by this process more than 22 litres of gas (Wöhler[†]).

Quantitative estimation of Carbon and its compounds. — The greater number of carbon-compounds are of organic nature, and contain hydrogen as well as carbon. Hence these two elements are generally estimated together, the process consisting in burning the compound with a large excess of oxide of copper, whereby the carbon is converted into carbonic acid, and the hydrogen into water. The carbonic acid is absorbed in a weighed apparatus containing caustic potash, and the excess of weight after the absorption, gives the quantity of carbonic acid produced by the combustion, $\frac{3}{11}$ of which is the weight of the carbon. The water is absorbed in a weighed apparatus containing dry chloride of calcium, and $\frac{1}{9}$ of its weight gives that of the hydrogen. The apparatus used for the analysis is described and delineated at page 277. For compounds which, like oxalic acid and sugar, are easily burned, the process of heating with oxide of copper affords a complete combustion of the carbon, and gives exact results; but when the proportion of carbon is very large, especially in fatty substances, which are not easy to burn, a different method must be adopted. Such bodies are either burned with chromate of lead, which at a red heat gives off free oxygen; or they are burned with oxide of copper, and towards the end of the process, a stream of oxygen is passed through the tube, either by placing at the closed extremity a quantity of perfectly dry chlorate of potash, and heating this salt, when the combustion of the organic substance by the oxide of copper appears to be nearly ended, — or better, by leaving that end of the tube open and connecting it with a gas-holder containing oxygen.[‡] In this manner, the last traces of carbon are effectually burned.

The quantity of *carbonic acid* in a carbonate may be easily determined by decomposing the carbonate with sulphuric or hydrochloric acid in the apparatus represented at page 438, the flask being weighed before and after the decomposition, and the quantity of carbonic acid estimated by the decrease of weight resulting from its evolution.

The quantity of carbonic acid contained in an aqueous solution, a mineral water for instance, may also be determined by mixing the solution with chloride of calcium and excess of ammonia, and leaving it for a day in a corked flask. The precipitated carbonate of lime is then collected on a filter, washed, dried, and weighed.

The amount of carbonic acid in a gaseous mixture not containing any other acid, is estimated by absorbing the carbonic acid with caustic potash. When the proportion of carbonic acid in the mixture is considerable, this end may be at-

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[*] Compt. rend. xxx. 48.

[†] Ann. Pharm. xci. 127.

[‡] For details of the apparatus, and the mode of proceeding, see H. Rose (*Hanb. d. Analyt. Chem.* ii. 956), and Gerhardt (*Traité de Chimie Organique*, i. 35). A very convenient apparatus for the purpose has lately been introduced by Dr. Hofmann.

tained by placing the gaseous mixture in a graduated tube over mercury and passing up into it a small coke ball containing a strong solution of caustic potash; but when the proportion is very small, as in the air, this method is not sufficiently delicate. Accurate results may, however, be obtained by drawing a considerable quantity of air, by means of an aspirator, through a series of potash-bulbs (p. 277) previously weighed, the quantity of air drawn through being of course carefully measured. Another method has recently been proposed by Dr. Pettenkofer; it consists in shaking up a quantity of the air in a closed vessel of known capacity, with an excess of lime-water of known strength, and then determining the quantity of lime remaining uncombined by means of a standard solution of oxalic acid. This method is very easy of execution, and gives the means of quickly determining the varying amount of carbonic acid in the several parts of an inhabited apartment at different times.

Carbonic oxide is most readily estimated and removed from a gaseous mixture by means of a solution of dichloride of copper (p. 478) in hydrochloric acid, which absorbs it as quickly and completely as potash absorbs carbonic acid. When no other gaseous compound of carbon is present, the quantity of this gas may also be determined by exploding it with oxygen, and absorbing the resulting carbonic acid by potash. For, since carbonic acid contains its own volume of oxygen, and carbonic oxide contains half its volume of oxygen, it follows, that if carbonic oxide be exploded with half its volume of oxygen, the volume of carbonic acid produced will be equal to that of the carbonic oxide consumed: hence the volume of carbonic oxide is equal to that of the gas which disappears by absorption with potash.

The quantity of *marsh gas* or *olefiant gas* in a gaseous mixture, not containing any other carbon compound, may be determined in a similar manner. Four volumes of marsh gas, C_2H_4, require for complete combustion 8 volumes of oxygen, and produce 4 volumes of carbonic acid. For the 2 atoms of carbon require 4 atoms of oxygen, to convert them into carbonic acid; and the 4 atoms of hydrogen require 4 atoms oxygen to convert them into water; therefore, in all, 8 atoms or 8 volumes (p. 130) of oxygen: moreover, the four volumes of oxygen required to consume the carbon produce 4 volumes of carbonic acid; hence the volume of gas which disappears by absorption with potash is equal to the original volume of the marsh gas.

By a similar calculation, it is found that 4 volumes of olefiant gas, C_4H_4, require 12 volumes of oxygen for complete combustion, and produce 8 volumes of carbonic acid: hence the volume of olefiant gas is equal to half the volume of gas removed by potash after the explosion. Olefiant gas may also be removed from a gaseous mixture by the introduction of a coke-ball saturated with anhydrous sulphuric acid or fuming oil of vitriol (p. 717).

For the methods of analyzing gaseous mixtures containing marsh gas and olefiant gas mixed with hydrogen, carbonic oxide, nitrogen, and other gases, I must refer to works in which the operations of gas-analysis are explained in detail.*

Oxalic acid is precipitated from its aqueous solution, or from solutions of the alkaline oxalates, by chloride of calcium, ammonia being added if necessary to render the solution neutral. The precipitated oxalate of lime is converted by ignition at a low red heat into carbonate, from the weight of which the quantity of oxalic acid may be calculated, each atom of carbonate of lime ($CaO . CO_2$) corresponding to 1 atom of anhydrous oxalic acid, C_2O_3:—

$$\underbrace{CaO . C_2O_3}_{\text{Oxalate of lime.}} = \underbrace{CaO . CO_2}_{\text{Carbonate of lime.}} + CO.$$

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* Bunsen's "Gasometry," translated by Roscoe, London, 1857; and Regnault, "Cours Elémentaire de Chimie," 2me. ed. Paris, tom. iv. pp. 73–103.

Consequently, 50 parts of carbonate of lime give 36 parts of anhydrous oxalic acid, C_2O_3, or 45 parts of the hydrated acid, C_2HO_4. In neutralizing the solution of an acid oxalate with ammonia, care must be taken to avoid excess of the alkali, as in that case carbonic acid will be absorbed from the air, and carbonate of lime will be precipitated as well as oxalate. It is better, however, to precipitate oxalic acid from its acid solutions with acetate of lime, as oxalate of lime is quite insoluble in acetic acid.

Oxalic acid may also be very exactly estimated by means of a solution of terchloride of gold. The gold is then reduced to the metallic state, water is decomposed, and the liberated oxygen converts the oxalic acid into carbonic acid: —

$$3C_2O_3 + AuCl_3 + 3HO = 6CO_2 + 3HCl + Au.$$

The decomposition may be performed in the flask apparatus already referred to (fig. 438, p. 186). It takes place at ordinary temperatures, but the liquid must be boiled at the end of the process to expel the last portions of carbonic acid. This method may be applied to the decomposition of all oxalates, whether soluble or insoluble in water, the insoluble oxalates being dissolved in hydrochloric acid. An excess of that acid in the concentrated state, however, greatly interferes with the action; the liquid should, therefore, be considerably diluted with water, and the action assisted by heat. The preceding equation shows that 2 atoms carbonic acid, CO_2, correspond to 1 atom of anhydrous oxalic acid, C_2O_3, or 11 parts by weight of carbonic acid to 9 parts of anhydrous oxalic acid.

Another mode of converting oxalic acid into carbonic acid, is by acting upon it, either in the free or combined state, with binoxide of manganese and sulphuric or hydrochloric acid (p. 438).

Oxalic acid, either free or combined, is resolved, by heating with an excess of strong sulphuric acid, into a mixture of equal volumes of carbonic acid and carbonic oxide. This method may also be applied to the estimation of oxalic acid, but it is not so accurate as the preceding.

Lastly, the quantity of oxalic acid in an oxalate may be estimated by burning the compound with oxide of copper (p. 771).

Estimation of Cyanogen. — The quantity of cyanogen in a soluble cyanide is easily determined by precipitation with nitrate of silver. The precipitated cyanide of silver is collected on a weighed filter and dried at 100° C. Every 134 parts of it contain 26 parts of cyanogen. Many insoluble cyanides may be decomposed by boiling with sulphuric or hydrochloric acid, hydrocyanic acid being evolved, and the metal remaining as sulphate or chloride, from the weight of which the quantity of cyanogen which has gone off may be calculated. Lastly, all cyanogen compounds whatever may be analyzed by burning with oxide of copper, in the manner already described.

BORON.

This element was formerly known only in the amorphous state, in which it is obtained by the action of potassium on boracic acid or borofluoride of potassium. But Wöhler and Deville* have lately obtained it in two distinct crystalline states, in one of which it bears a close resemblance to diamond, and in the other to graphite.

The first of these crystalline forms of boron is obtained by decomposing boracic acid with aluminium at a high temperature. When 80 grammes of aluminium in thick lumps, and 100 grammes of fused or pulverized boracic acid, are heated together in a crucible lined with charcoal to about the melting point of nickel for five hours, there are found on breaking the crucible after cooling, two distinct layers, one of which is glassy, and consists of boracic acid and alumina, while the other is metallic, tumefied, has an iron-grey lustre, and consists of aluminium

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* Compt. rend. xliii. 1088.

mixed with a considerable quantity of crystallized boron, some of the crystals being distinctly visible at the surface. The aluminium is dissolved out by strong boiling soda-ley, and the residual boron is freed from iron by digestion in hydrochloric acid, and from traces of silicon by a mixture of nitric and hydrofluoric acids. It is still, however, mixed with laminæ of alumina, which must be carefully picked out.

The pure product thus obtained is *diamond-boron*, mixed, however, with a small quantity of graphitoïdal boron, which latter being very light, may be removed by suspension in water. Diamond-boron forms transparent crystals, having a honey-yellow or garnet-red colour, due to the presence of small quantities of foreign substances; it has hitherto been obtained only in confused aggregates of small crystals. In lustre and refractive power, it is scarcely inferior to the diamond; and is one of the hardest bodies known, inasmuch as it scratches corundum, and even the diamond itself. It does not fuse at the heat of the oxyhydrogen blowpipe, and withstands the action of oxygen even when strongly heated; but it is slightly oxidized at the temperature at which the diamond burns, a film of boracic acid being then formed, which protects the remainder of the crystals from oxidation. Heated to redness in chlorine gas, it burns and produces chloride of boron. Heated by the blowpipe between two pieces of platinum-foil, it forms a fusible boride of platinum. It is not attacked by acids at any temperature, but when heated to redness with bisulphate of potash, it is converted into boracic acid. It is not attacked by a strong boiling solution of caustic soda; but hydrate and carbonate of soda dissolve it slowly at a red heat. Nitre does not appear to act upon it sensibly at that temperature.

Graphitoïdal Boron is produced in small quantity simultaneously with diamond-boron by the process above described. But it is obtained much more readily by treating borofluoride of potassium with aluminium, adding as a flux a mixture of equal parts of chloride of potassium and chloride of sodium; in this manner, small masses of boride of aluminium are obtained, which, when digested in hydrochloric acid, leave graphitoïdal boron. The laminæ of this substance are often hexagonal: they have a slight reddish colour, and the form and lustre of native graphite. They are always opaque.

Amorphous boron is formed in the preparation of diamond-boron when a small globule of aluminium comes in contact with a large quantity of boracic acid, so that the boron does not dissolve in the aluminium as fast as it is set free. In this case, after the aluminium has been removed by the use of caustic soda and hydrochloric acid, the boron remains as an amorphous mass of a light chocolate colour, and exhibiting the properties which have long been known as belonging to boron. When the amorphous boron is collected on a filter, the portion which remains adhering to the filter, burns, when the paper is dried and set on fire, very easily and with an intense light; graphitoïdal boron, under the same circumstances, does not burn at all.

Boracic acid.—According to A. Vogel,* the brown colour imparted to turmeric by boracic acid is distinguished from that produced by alkalies, by not being destroyed by the action of acids. Thus, when an alcoholic tincture of turmeric diluted with water till its colour becomes light yellow, is added to a concentrated solution of borax, the yellow colour is changed to brown by the alkaline reaction of the salt, but on adding a certain quantity of sulphuric acid, the yellow colour is restored. A larger quantity of sulphuric acid sets free the boracic acid, and again produces a brown colour; which, however, does not disappear on further addition of the acid.

For detecting small quantities of boracic acid in solutions, mineral waters, for instance, H. Rose† acidulates the liquid with hydrochloric acid, dips a strip of

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* Repert. Pharm. iii. 178.

† Handb. d. Analyt. Chem. i. 919, 946.

turmeric paper into the liquid, and then leaves it to dry; if boracic acid is present, the part of the paper which has been immersed in the liquid, assumes a red-brown colour.

Boracic acid being but a weak acid, its salts are often decomposed by water. A concentrated solution of borax, added to nitrate of silver, throws down white borate of silver; but a dilute solution — which in fact consists of borate of water mixed with free soda—forms a brown precipitate of oxide of silver. If to a strong solution of borax, an alcoholic tincture of litmus reddened by acetic acid be added in such quantity that the red colour is nearly but not quite destroyed, and the liquid be then diluted with water, the red colour is immediately changed to blue (H. Rose).*

Nitride of Boron, BN. — This compound was discovered by Balmain,† who at first regarded it as capable of uniting with metals and forming compounds analogous to the cyanides, but afterwards found that all these supposed metallic compounds were one and the same substance, viz. nitride of boron, without any appreciable amount of metal. Balmain obtained this substance by heating boracic acid with cyanide of potassium or cyanide of zinc, or with cyanide of mercury and sulphur. It has since been more completely investigated by Wöhler,‡ who prepares it by heating to bright redness, in a porcelain or platinum crucible, a mixture of 2 pts. of dried sal-ammoniac and 1 pt. of pure anhydrous borax. The product is a white porous mass, which is pulverized and washed with water to free it from chloride of sodium. The final washings must be made with boiling-water acidulated with hydrochloric acid. Boracic acid may be used in the preparation instead of borax. Wöhler formerly obtained the nitride of boron by igniting anhydrous borax with ferrocyanide of potassium.

Nitride of boron is a white amorphous powder, tasteless, inodorous, soft to the touch, insoluble in water, infusible, and non-volatile. Heated at the point of the blowpipe-flame, it burns with a bright greenish-white flame. It easily reduces the oxides of copper and lead, giving off nitrous fumes. Heated in a current of aqueous vapour, it yields ammonia and boracic acid: —

$$BN + 3HO = BO_3 + NH_3.$$

Alkalies and the greater number of acids, even in the state of concentrated solution, have no action on nitride of boron; strong sulphuric acid, however, with the aid of heat, ultimately converts it into ammonia and boracic acid. Fuming hydrofluoric acid converts it into borofluoride of ammonium. Nitride of boron undergoes no alteration when heated in a current of chlorine. When fused with hydrate of potash, it gives off a large quantity of ammonia. With anhydrous carbonate of potash, it yields borate and cyanate of potash: —

$$BN + 2(KO.CO_2) = BO_3.KO + C_2NO.KO.$$

It does not decompose carbonic acid, even at the highest temperatures. Marignac§ found also that nitride of boron does not form definite compounds with metals, and that its formula is BN.

Estimation of Boron and Boracic acid.—The most exact method of estimating boron is to convert it into borofluoride of potassium, $KF.BF_3$. If the substance to be treated is free boracic acid or an alkaline borate, a sufficient quantity of potash is first added, then an excess of pure hydrofluoric acid (so that the escaping vapours may redden litmus), and the mixture is evaporated to dryness in a silver or platinum vessel. The dry saline mass is then stirred up with a solution of

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* Ann. Ch. Pharm. lxxxiv. 216.

† Phil. Mag. [3], xxi. 170; xxii. 467; xxiii. 71; xxiv. 19.

‡ Ann. Ch. Pharm. lxxiv. 70.

§ Ann. Ch. Pharm. lxxix. 247

acetate of potash containing 20 per cent. of the salt; then, after a few hours, thrown on a weighed filter, and the precipitate washed, first with the solution of acetate of potash, till the filtrate no longer gives a precipitate with chloride of calcium, then with strong alcohol, and dried at 100°. The residue consists of borofluoride of potassium, every 124·7 parts of which correspond to 34·9 of boracic acid and 10·9 of boron.

The twenty per cent. solution of acetate of potash dissolves chloride of potassium and phosphate of potash, and likewise the sulphate, though less readily; it also dissolves soda-salts; the fluoride, however, slowly. Any other bases which may be combined with the boracic acid, must be previously separated by boiling or fusing the compound with carbonate of potash (A. Stromeyer.)*

Boracic acid cannot be estimated in its aqueous solution by simple evaporation to dryness, since a large quantity of it goes off with the watery vapour.

SILICON.

Silicon, like boron, may be obtained in three states analogous to the amorphous, graphitoïdal, and diamond forms of carbon. The amorphous variety is that which Berzelius obtained by the action of potassium on silicofluoride of potassium (p. 289). H. Ste-Claire Deville† prepares amorphous silicon by passing the vapour of the chloride over red-hot sodium in an atmosphere of dry hydrogen. The silicon thus obtained exhibits, after washing and drying at a moderate heat, the properties described by Berzelius.

Silicon is fusible — its melting point being intermediate between the melting points of steel and cast iron; but when heated in the air, it quickly becomes encrusted with a coating of silicic acid, which being exceedingly difficult of fusion, causes the silicon also to appear infusible.

Graphitoïdal Silicon.—This modification of silicon was first obtained by Deville in preparing aluminium by the electrolysis of the double chloride of aluminium and sodium. The first portions of aluminium thus obtained are contaminated with silicon derived from the charcoal electrodes; and when this alloy of silicon and aluminium is treated with hydrochloric acid, the silicon remains undissolved in the form of shining metallic scales resembling graphite. A more productive method of obtaining this variety of silicon is given by Wöhler.‡ It consists in mixing aluminium with between 20 and 40 times its weight of silico-fluoride of potassium, and heating the mixture in a Hessian crucible to the melting point of silver. A metallic button is thus obtained, which, when treated successively with hydrochloric and hydrofluoric acids, yields graphitoïdal silicon, partly in isolated hexagonal tables, the edges of which are often curved. This graphitoïdal silicon exhibits all the properties ascribed by Berzelius to silicon which has been strongly heated. Its density is 2·49, which is less than that of quartz (from 2·6 to 2·8). It may be heated to whiteness in oxygen gas without burning or undergoing any alteration in weight; but when heated to redness with carbonate of potash, it decomposes the carbonic acid, with vivid emission of light and formation of silica. It is not attacked by any acid. A strong solution of potash or soda dissolves it slowly, with evolution of hydrogen. Heated to commencing redness in dry chlorine gas, it burns completely, and forms chloride of silicon.

Octohedral or Diamond Silicon. — When vapour of chloride of silicon is passed over aluminium kept in a state of fusion in an atmosphere of hydrogen, part of the aluminium is converted into chloride, which volatilizes, and the silicon thereby separated dissolves in the remaining aluminium, which thus becomes more and more saturated with silicon; and at length a point is attained at which the excess of silicon separates from the melted aluminium in large beautiful needles,

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* Ann. Ch. Pharm. c. 82.

† Ann. Chem. Phys. [3], xlix. 62.

‡ Compt. rend. xlii. 48.

having a dark iron-grey colour, reddish by reflected light, and exhibiting iridescence like that of iron-glance. These crystals are derived from the regular octohedron, and often, like the diamond, exhibit curved faces; they are very hard, and are capable of scratching and of cutting glass (Deville).

Atomic weight of Silicon. — It is still a disputed question whether the atomic weight of silicon should be 21·35 or 14·1, and accordingly, whether the formula of the oxide, chloride, &c., should be SiO_3, $SiCl_3$, &c., or SiO_2, $SiCl_2$, &c. The vapour-density of the chloride, 5·939 according to Dumas, is in favour of the formula $SiCl_2$, which gives a condensation to 2 volumes (or rather Si_2Cl_4, giving a condensation to 4 vols.), whereas the formula $SiCl_3$ would involve the very unusual condensation to 3 volumes. An argument in favour of this latter formula has been drawn from the difference between the boiling points of the bromide and chloride of silicon ($153° - 59°\,C = 94 = 3 \times 32$ nearly), inasmuch as the earlier researches of H. Kopp had led him to conclude that the boiling points of analogous chlorides and bromides generally differ by multiples of 32° C. Kopp has, however, more recently shown that this law is very far from being a general expression of observed results, and that the difference, 23·5° or its multiples, occurs quite as frequently. Now the difference 94 between the boiling points of bromide and chloride of silicon, is just $4 \times 23{\cdot}5$, and is therefore so far consistent with the formulæ Si_2Br_4 and Si_2Cl_4.

Colonel Yorke[*] has endeavoured to determine the formula of silicic acid, by ascertaining the quantity of carbonic acid displaced from excess of an alkaline carbonate by fusion with a given weight of silica. Experiments with carbonate of potash gave, as a mean result, 30·7 for the equivalent of silicic acid, agreeing with the formula SiO_2 ($14{\cdot}1 + 2 \times 8 = 30{\cdot}1$). Experiments with carbonate of soda gave 21·3 for the equivalent of silicic acid, agreeing nearly with half that which is represented by the formula SiO_3 ($21{\cdot}35 + 3 \times 8 = 45{\cdot}35$). Experiments with carbonate of lithia gave the number 14·99, agreeing nearly with the formula SiO. By fusing 23 parts of silica with 54 parts of carbonate of soda, dissolving the fused mass in water, and evaporating the solution in vacuo, a crystallized salt was formed containing (besides 5 per cent. of carbonate of soda) the salt $NaO.SiO_2 + 7HO$. These results seem to show that silicon is capable of uniting with oxygen in more than one proportion, a conclusion in accordance with the results obtained by other experimenters.

Wöhler and Buff,[†] by heating silicon to low redness in a current of dry hydrochloric acid gas, have obtained a new chloride of silicon, which is a mobile fuming liquid, more volatile than the terchloride. Water decomposes this liquid, forming hydrochloric acid, and a new oxide of silicon, which is a white substance, slightly soluble in water, but dissolving very easily in alkalies,—even in ammonia, with evolution of hydrogen and formation of silicic acid. When heated in the air, it burns with a white flame. This compound is evidently a lower oxide of silicon, but its exact composition has not yet been determined.

Fuchs has obtained two hydrates of silicic acid; one containing between 9·1 and 9·6 per cent. of water, the other between 6·6 and 7 per cent. The former might be denoted by either of the formulæ, $2SiO_3.HO$ or $3SiO_2.HO$, according to the atomic weight of silicon chosen; but the latter agrees only with the formula, $4SiO_2.HO$.[‡]

The true formula of silicic acid and atomic weight of silicon must then be considered as still undecided; the balance of evidence seems, however, to incline in favour of the formula, SiO_2, making the atomic weight of silicon 14·1. The analogy between silicic acid and titanic acid points to the same conclusion.

Chloride of Silicon and Hydrogen, $Si_2Cl_8.2HCl$. — This is the compound which Wöhler and Buff obtained by heating crystalline silicon in a current of dry hydrochloric acid gas. It is a colourless, very mobile liquid, of sp. gr. 1·65, and

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[*] Proceedings of the Royal Society, viii. 140.

[†] Compt. rend. xliv. 834.

[‡] Ann. Ch. Pharm. lxxxii. 119.

boiling at 42° C. It has a very pungent odour, and fumes strongly in the air. Its vapour is as inflammable as ether-vapour, and burns with a faint greenish flame, diffusing vapours of silica and hydrochloric acid. When passed through a red-hot tube, it is decomposed, yielding hydrochloric acid, terchloride of silicon, and a specular deposit of amorphous silicon. The compound is decomposed by water with formation of a corresponding oxide.

The compounds $Si_2Br_3.2HBr$, and $Si_2I_3.2HI$, are obtained in a similar manner. The former is liquid, the latter solid, at ordinary temperatures.

Hydrated Oxide of Silicon.—$Si_2O_3.2HO$, is formed by the action of water on either of the preceding compounds, but most easily from the chloride. It is a snow-white amorphous, very bulky powder, which floats on water. It is insoluble in all acids except hydrofluoric acid. Alkalies, even ammonia, dissolve it readily, with evolution of hydrogen and formation of an alkaline silicate.

It may be heated to 300° C. without alteration; but at higher temperatures, it glows brightly, and gives off spontaneously inflammable hydrogen gas (containing siliciuretted hydrogen.)

A lower oxide of silicon (SiO?) and the corresponding chloride appear also to exist.*

Siliciuretted Hydrogen. A remarkable gaseous compound of silicon and hydrogen is produced when a bar of aluminium containing silicon is connected with the *positive* pole of a Bunsen's battery of 8 to 12 cells, and made to dip into a solution of chloride of sodium. The aluminium then dissolves in the form of chloride, a considerable quantity of gas is evolved at its surface, and many of the gas-bubbles, as they escape into the air, take fire spontaneously, burning with a white light and diffusing a white fume. When the gas is collected in a tube over water, and bubbles of oxygen are passed up into it, each successive bubble produces at first a brilliant white light and a copious white fume; but this effect gradually diminishes in intensity, and at last the remaining gas will no longer burn spontaneously by contact with oxygen. This residual gas is hydrogen; the spontaneously inflammable gas, which forms but a small portion of the mixture, is siliciuretted hydrogen. When the gaseous mixture is made to escape from a glass jar provided with a stop-cock, it burns in a jet, and deposits silica round the orifice. A piece of white porcelain held in the flame, becomes stained with a brown deposit of silicon; and if the gas be made to pass through a narrow glass tube, and heated till the glass softens, a deposit of silicon is likewise obtained, and the gas which issues from the tube is no longer spontaneously inflammable. The compound has not yet been analyzed quantitatively.

The formation of siliciuretted hydrogen appears to be due to a secondary action accompanying the electrolysis of the saline solution. The aluminium, forming the positive pole of the battery, combines with the chlorine and dissolves; but the quantity of aluminium removed is about one-fourth greater than that which is equivalent to the quantity of chlorine eliminated from the solution. This excess of aluminium is found to be removed in the form of alumina, uniting with oxygen derived from the water of the solution. The equivalent quantity of hydrogen is of course evolved, and part of it enters into combination with the silicon contained in the aluminium. The compound has not yet been obtained by a purely chemical reaction; but it has been observed that the hydrogen evolved, when aluminium dissolves in hydrochloric acid, burns with a brighter flame than pure hydrogen, and yields a small deposit of silica (Wöhler and Buff.)†

Estimation of Silicon and Silicic acid.—When silica exists in solution, it may be completely separated from all the other substances present, by acidulating the solution with hydrochloric acid, evaporating to dryness, and boiling the residue with water containing hydrochloric acid, which will dissolve everything excepting

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* Ann. Ch. Pharm., Oct. 1857, p. 94.

† Ann. Ch. Pharm. ciii. 218.

the silica. The residue may then be dried, ignited, and weighed. The completeness of this separation depends on the perfect drying of the silica before it is boiled with the acidulated water. Now, to ensure this complete dryness, the silica must be heated somewhat above the temperature of the water-bath, the drying being completed on a sand-bath or over a lamp. In doing this, it sometimes happens that too much heat is applied, and, in that case, certain other substances, especially alumina and oxide of iron, may also be rendered insoluble in the dilute acid. To obviate this source of error, the dried residue must be moistened all over with strong hydrochloric acid, then left to stand for half an hour, and afterwards boiled with water. Everything will then dissolve excepting the silica.

Analysis of Silicates. — Some natural silicates, cerite, for example, are completely decomposed by hydrochloric acid. In that case, it is sufficient to boil the pulverized mineral with strong hydrochloric acid as long as anything continues to be dissolved; then evaporate to complete dryness, and treat the residue as above. The liquid filtered from the insoluble silica contains the bases of the mineral, which may be separated and estimated by methods already described.

Silicates which, like felspar, resist the action of hydrochloric acid, are decomposed by fusion with an alkaline carbonate. The mineral, very finely powdered, is mixed in a platinum crucible with three or four times its weight of dry carbonate of soda; the platinum crucible, placed within an earthen crucible lined with magnesia, and heated to bright redness in a furnace for about twenty minutes; the fused mass, when cold, removed from the crucible by digestion in dilute hydrochloric acid with the aid of heat; the whole evaporated to dryness; and the silica separated, and the bases determined as above. Some silicates, zircon for example, resist the action of alkaline carbonates, and must be decomposed by fusion with hydrate of potash or soda in a silver crucible.

By this process, not only the silica, but all the bases of silicate may be determined, excepting the alkalies. To determine these, the mineral, reduced to an almost impalpable powder, is very intimately mixed with five times its weight of pure carbonate of lime, and the mixture exposed in a platinum crucible, protected as above, to the strongest heat of an air-furnace for about half an hour. The mass, which is not fused, but sintered together, is then digested in dilute hydrochloric acid; the silica separated as before; the greater part of the lime and likewise the bases of the silicate precipitated by carbonate of ammonia and free ammonia; the filtrate evaporated to dryness, and the ammoniacal salts expelled by ignition; the residue redissolved in water; the remainder of the lime precipitated by oxalate of ammonia; and the ammoniacal salts again expelled by evaporation and ignition. The residue then contains nothing but the chlorides of the fixed alkalies and magnesia, if that substance was contained in the mineral. Carbonate of baryta may also be used instead of carbonate of lime, and the excess of baryta removed by sulphuric acid.

Another method of obtaining the alkalies in a silicate, is to decompose it with hydrofluoric acid aided by a gentle heat. The acid must be added by small portions to the finely pulverized mineral contained in a platinum dish, till the action ceases and the whole is reduced to a pasty mass. This mass is then heated with strong sulphuric acid, which expels fluoride of silicon and hydrofluoric acid; the residue is heated to low redness to expel the excess of sulphuric acid; the dry mass, when cold, moistened with strong hydrochloric acid, and, after standing for about half an hour, digested with water. The whole then dissolves, provided the decomposition by the hydrofluoric acid has been complete. The solution contains the alkalies and the other bases in the state of sulphates.

SULPHUR.

Allotropic Modifications of Sulphur (p. 292). — Among the various modifications of sulphur, there are, according to Berthelot,* two principal states which are more stable than the rest, and are, in fact, the limits to which all the others may be reduced. These are, first, the *octohedral*, or *electro-negative* sulphur, which acts as a supporter of combustion, and the *electro-positive*, or combustible sulphur, which is generally amorphous and insoluble in bisulphide of carbon, alcohol, &c.

Allied to octohedral sulphur are two conditions of inferior stability, viz., the prismatic variety, which crystallizes from melted sulphur, and the soft emulsionable sulphur (milk of sulphur), precipitated from the solution of an alkaline polysulphide by the action of acids. Both these varieties of sulphur are soluble in bisulphide of carbon, and change spontaneously into octohedral sulphur after a certain time.

Electro-positive sulphur, properly so called, is that which is obtained when sulphur separates from any of its compounds with oxygen, chlorine, bromine, &c., the chloride or bromide yielding the most stable variety. It is amorphous and insoluble in solvents properly so called, that is to say, in liquids which do not act upon it chemically, such as water, alcohol, ether, bisulphide of carbon, &c.

To this electro-positive sulphur are allied several modifications more or less distinct, which may perhaps be reduced to three principal varieties, all amorphous, but less stable than the one just mentioned, viz., the soft sulphur precipitated from solutions of the hyposulphites; the insoluble sulphur obtained by exhausting flowers of sulphur with alcohol and bisulphide of carbon; and the insoluble sulphur obtained by exhausting with bisulphide of carbon the soft sulphur produced by the action of heat. These varieties are distinguished one from the other by the greater or less facility with which they are transformed into soluble crystallizable sulphur, either by a temperature of 100° C., or by contact with certain electro-positive bodies, such as the alkalies and their sulphides, an alcoholic solution of hydrosulphuric acid, &c. By the contrary influences, that is to say, by contact with bodies having a decided electro-negative character, they may all be reduced to the most stable insoluble variety, viz., that which is deposited from the chloride or bromide of sulphur.

The particular modification which sulphur assumes when separated from any of its compounds, depends essentially on the nature of that compound. It is altogether independent of the state of the sulphur previous to combination, and likewise of the reagent which produces the separation, provided that reagent has neither a decided electro-positive character, such as the alkalies, nor a decided electro-negative or oxidizing character, and provided that it acts rapidly and without any considerable evolution of heat. The influence of these latter conditions, is due chiefly to the unequal stability of the several modifications of sulphur. Of all these varieties, the octohedral sulphur is the most stable, and that to which all the others, even the most electro-positive, tend to return, especially under the influence of heat. (Berthelot).

Sulphur, deposited at the positive pole of the voltaic battery in the electrolysis of an aqueous solution of hydrosulphuric acid, is soluble in bisulphide of carbon and crystallizable; but that which is deposited at the negative pole in the electrolysis of sulphurous or sulphuric acid, is insoluble in bisulphide of carbon. (Berthelot†).

Magnus‡ obtained a *black* modification of sulphur by repeatedly heating sulphur to 300° C., cooling suddenly, and exhausting with bisulphide of carbon; and this black sulphur, heated to a temperature between 130° and 150°, passed into a

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* Ann. Ch. Phys. [3], xlix. 430.

† Pogg. Ann. xcii. 308.

‡ Ann. Ch. Pharm. ci. 58.

red modification. According to Mitscherlich, however, pure sulphur does not exhibit these modifications, but when sulphur is melted with small quantities of fatty matters, various highly coloured products are obtained. Even the grease imparted by touching sulphur with the fingers, is sufficient to alter its colour considerably when melted.

Vapour of sulphur, when it comes in contact with cold bodies, condenses in the form of *utricles*, that is to say, of globules composed of a soft external pellicle filled with liquid sulphur. They sometimes rètain their liquid form for a considerable time. This utricular condition has also been observed in selenium, iodine, phosphorus, and arsenious acid. (Brame*).

Respecting the melting point of sulphur, the observations of different experimenters vary from 104·5° to 112·2° C. This discrepancy is attributed by Professor Brodie† to the fact that the melting point of sulphur varies according to its allotropic state. According to the observations of that chemist, rhombic or octohedral sulphur (crystallized from bisulphide of carbon, alcohol, or benzol) melts at 114·5° C.; but, between 100° and 114·5°, it is transformed into the oblique prismatic modification, which melts at 120°, and if not afterwards more strongly heated, solidifies at nearly the same point. If, however, its temperature be further raised, it does not solidify till cooled to 111·5°, and if it be then heated, melts at a point very little higher. In fact, above 120°, sulphur begins to pass into the plastic state, which is more fusible. The variety insoluble in bisulphide of carbon has a melting point considerably above 120°. The gradual loss of transparency of the prismatic sulphur crystallized from fusion, arises, according to Brodie, from the hardening of plastic sulphur mechanically enclosed within the crystals. When crystals which have thus lost their transparency, are digested in bisulphide of carbon, a portion always remains undissolved. If sulphur which has been fused and strongly heated, be suddenly cooled by a mixture of solid carbonic acid and ether, it solidifies in a hard, perfectly transparent mass, which becomes soft and elastic at ordinary temperatures. This appears. indeed, to be the solid state of plastic sulphur.

Formation of Anhydrous Sulphuric acid.—When a dry mixture of 2 vols. sulphurous acid and 1 vol. oxygen or atmospheric air, is passed through a red-hot glass tube containing certain metallic oxides, *e. g.* cupric, ferric, or chromic oxide, the gases unite and produce dense white fumes of anhydrous sulphuric acid. A mixture of the oxides of copper and chromium induces the combination with peculiar facility. These oxides appear to be capable of inducing the combination of unlimited quantities of sulphurous acid and oxygen. Spongy metallic copper produces the same effect when heated, but not till the copper has become oxidized. Clean polished platinum foil, or spongy platinum, produces the combination considerably below a red heat, but not at ordinary temperatures. (Wöhler‡).

Sulphide of Nitrogen (p. 309).—This body was discovered by Soubeiran, who assigned to it the formula NS_3; but it has since been more minutely examined by Fordos and Gélis,§ who have shown that its true formula is NS_2. The best mode of preparing it is to pass dry ammoniacal gas into a solution of protochloride of sulphur, SCl, in eight or ten times its volume of bisulphide of carbon. Crystals of sal-ammoniac are then deposited, and the solution becomes darker in colour, and deposits cochineal-coloured flakes, which soon decompose and turn brown. An excess of ammonia decomposes this brown compound. The current of gas must be continued till the solution acquires an orange-yellow colour, and contains only very slightly coloured flakes, which may be separated by filtration. The filtrate, when left to evaporate, deposits crystals of sulphur, while the sulphide of

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* Compt. rend. xxix. 657; xxxiii. 538, 579.

† Proceedings of the Royal Society, vii. 24.

‡ Ann. Ch. Pharm, lxxxi. 255.

§ Compt. rend. xxxi. 702.

nitrogen remains in the mother liquid, and may be obtained by further evaporation of the decanted liquid. The reaction is as follows: —

$$3SCl + 4NH_3 = NS_2 + S + 3NH_4Cl.$$

At the same time, however, there are a number of intermediate products formed (the brown flocculent matters above-mentioned), consisting of compounds of sulphide of nitrogen with chloride of sulphur, viz., $SCl . NS_2$; $SCl . 2NS_2$; and $SCl . 3NS_2$; but these are all ultimately decomposed by excess of ammonia. Sulphide of nitrogen forms similar compounds with dichloride of sulphur, S_2Cl.

Sulphide of nitrogen is insoluble in water, slightly soluble in alcohol, wood-spirit, ether, and oil of turpentine; bisulphide of carbon dissolves it to the amount of 15 parts in 1000, and the solution deposits the compound in small elongated prisms derived from the right rhomboïdal prism, and terminated with dihedral summits; they are transparent and of a golden yellow colour. The solution must, however, be evaporated immediately, for it decomposes after a short time, yielding hydrosulphocyanic acid, and a yellow substance like that which is commonly called sulphocyanogen. Water slowly decomposes sulphide of nitrogen, yielding free ammonia, together with hyposulphurous and trithionic acids: —

$$4NS_2 + 15HO = NH_4O . S_2O_2 + 2(NH_4O . S_3O_5) + NH_3.$$

Protosulphide of Carbon, CS.—This compound is obtained: 1. By passing the vapour of bisulphide of carbon over spongy platinum or pumice-stone heated to redness; sulphur is then deposited, and the protosulphide liberated in the form of gas. 2. In the preparation of the bisulphide, and simultaneously therewith. 3. By decomposing the vapour of the bisulphide at a red heat by means of lamp-black, wood-charcoal, and especially by animal charcoal in fragments. 4. By decomposing the vapour of the bisulphide at a red heat with hydrogen. 5. By calcining sulphide of antimony with excess of charcoal. 6. By the action of carbonic oxide on hydrosulphuric acid at a red heat! —

$$CO + HS = HO + CS.$$

7. By the action of sulphurous acid, or chloride of sulphur, on olefiant gas at a red heat. 8. In the decomposition of sulphocyanogen by heat, &c.

The first process yields the gas tolerably pure; that which is obtained by the other processes is mixed with hydrosulphuric acid, and carbonic oxide. It is purified by passing it rapidly through solutions of acetate of lead, and dichloride of copper dissolved in hydrochloric acid, and then dried and collected over mercury.

Protosulphide of carbon is a colourless gas, having a strongly ethereal odour, resembling that of the bisulphide, but not disagreeable. When breathed in too large a quantity, it appears to be powerfully anæsthetic. It burns with a fine flame, producing carbonic and sulphurous acids, and a little sulphur. Its density is somewhat greater than that of carbonic acid. It does not liquefy at the temperature of a mixture of ice and salt. Water dissolves nearly its own volume of this gas; but decomposes it somewhat quickly into hydrosulphuric acid and carbonic oxide. It is scarcely more soluble in alcohol or ether. It is not absorbed by a solution of dichloride of copper. Acetate of lead is slowly blackened by it. It is rapidly decomposed by solutions of caustic alkalies. With lime-water, it yields sulphide of calcium, and a volume of carbonic oxide equal to its own: —

$$CaO + CS = CaS + CO.$$

This reaction establishes its composition, which is further confirmed by the fact, that, when exploded with oxygen, it yields equal volumes of carbonic and sulphurous acids. At a red heat, it is slightly decomposed: 1. By spongy platinum; 2. By aqueous vapour, into HS and CO; 3. More readily by hydrogen into HS and a hydrocarbon; 4. Completely by copper, yielding sulphide of copper, and graphitoïdal carbon; 5. By an equal volume of chlorine in sunshine, with formation of products not yet examined. (Baudrimont.*)

Bisulphide of Carbon.—By the action of nascent hydrogen (generated by slowly decomposing hydrochloric acid with zinc) upon bisulphide of carbon, Girard† has obtained a compound, CHS, which is neutral to vegetable colours, has a powerful odour, is insoluble in water, dissolves sparingly in alcohol, ether, and rock-oil, more readily in chloroform and bisulphide of carbon, but most readily in benzol; crystallizes from its solutions in square prisms; sublimes undecomposed at 150° C. in long needles; but decomposes at 200°. It is not altered by alkalies; dissolves in warm hydrochloric acid; and is decomposed by nitric and by strong sulphuric acids. It forms crystalline compounds with nitrate of silver, and with the chlorides of platinum, gold, and mercury.

Bisulphide of carbon, enclosed with water in a sealed tube, and heated for three or four hours to 150° C., is resolved into carbonic and hydrosulphuric acids. Many metallic oxides and salts, treated in a similar manner with bisulphide of carbon, yield carbonic acid and a metallic sulphide. (Schlagdenhauffen.‡)

Quantitative estimation of Sulphur and its compounds.—Sulphur is almost always estimated in the form of sulphuric acid. To determine the quantity of sulphur in a metallic sulphide, the compound is heated with nitric acid, aqua-regia, or sometimes with a mixture of hydrochloric acid and chlorate of potash, till the metal is oxidized, and the sulphur converted into sulphuric acid. The solution is then treated with chloride of barium or nitrate of baryta, and the precipitated sulphate of baryta collected on a filter, washed, dried, and ignited. Before adding the baryta-solution, however, the liquid must be considerably diluted with water, because the nitrate and chloride of barium are themselves insoluble in strong nitric and hydrochloric acids. The liquid is then boiled, and afterwards left to stand till the precipitate has completely settled down; after which the clear liquid is first passed through the filter, and then the precipitate thrown upon it; if the precipitate be poured upon the filter before it has settled down, it will be sure to run through. As the oxidation of the sulphur is very slow, the metal being completely oxidized and dissolved long before it, and a portion of the sulphur separated in the free state, it is sometimes convenient to collect this portion on a small weighed filter, determine its amount by direct weighing, and afterwards estimate the dissolved portion as above.—In the sulphides of gold and platinum, from which the sulphur is completely expelled by ignition, its quantity may be at once determined by weighing the residual metal. The sulphides of the alkali-metals and alkaline earth-metals are sometimes analyzed by decomposing them with hydrochloric acid, receiving the evolved hydrosulphuric acid in a solution of acetate of lead, oxidizing the precipitated sulphide of lead with fuming nitric acid, weighing the sulphate of lead thus produced, and thence calculating the quantity of sulphur.

The sulphur in organic compounds may likewise be estimated by oxidizing the compound with fuming nitric acid, and precipitating the resulting sulphuric acid with a baryta-solution. Another method, given by Dr. W. J. Russell,§ is to burn the substance in a combustion-tube with oxide of mercury, carbonate of soda being added to take up the sulphuric acid produced, and a small bent tube dipping under water fitted into the open end of the combustion-tube, so that any acid vapours that escape may be condensed in the water. At the end of the combustion, this liquid is acidulated with hydrochloric acid; the tube washed out with the acid solution; the liquid filtered; and the sulphuric acid precipitated by chloride of barium.

The quantity of *sulphuric acid* in a soluble sulphate is estimated by precipi-

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* Compt. rend. xliv. 1000.

† Compt. rend. xliii. 396.

‡ J. Pharm. [3], xxix. 401.

§ Chem. Soc. Qu. J. xi. 212.

tating the aqueous solution with chloride of barium. Some sulphates which are insoluble in water may be dissolved in hydrochloric or nitric acid, and the baryta-solution then added. The sulphates of lime, strontia, and lead may be decomposed by boiling with a solution of carbonate of soda (p. 736), and the sulphuric acid precipitated by chloride of barium from the filtered solution, previously acidulated with nitric or hydrochloric acid. Sulphate of baryta must be decomposed by fusion in a platinum crucible with three times their weight of carbonate of soda; the fused mass digested in water; the filtered soda-solution acidulated; and the sulphuric acid precipitated as above.

Sulphurous and hyposulphurous acid may be estimated by oxidation with nitric acid, whereby they are converted into sulphuric acid, or by Bunsen's iodometric method (p. 801).

SELENIUM.

Preparation of Selenium (p. 311). — This element is extracted from natural selenides, and principally from the seleniferous ores of the Harz, by the following process: — The pulverized ore is treated with hydrochloric acid, to remove the earthy carbonates with which it is mixed. The residue, after being well washed and dried, is mixed with its own weight of black flux, and calcined for an hour at a red heat. Selenide of potassium is thus formed, which is separated by washing the cooled and rapidly pulverized residue with boiling water. A brown-red solution is thus obtained, and the insoluble matter which remains on the filter retains the metals (copper, lead, and silver) which were combined with the selenium. The solution of selenide of potassium oxidizes gradually on exposure to the air, potash being formed, and the selenium collecting in a grey mass, which is carefully washed, dried, and distilled.

When the selenium contains sulphur, it is converted into seleniate and sulphate of potash by calcination with a mixture of nitre and carbonate of potash. The calcined mass is dissolved in hydrochloric acid, and the liquid saturated with sulphurous acid gas, and heated to the boiling point. The selenic acid is thereby reduced, and the selenium precipitated in red flakes, while the sulphate of potash remains in solution. (Wohler.*)

Modifications of Selenium. — Berzelius found that selenium solidifies in the amorphous state by sudden, and in the crystalline state by slow cooling. Hittorff finds that crystalline (or granular) selenium melts at 211·5° C. (412·6° F.), without previous softening. The mass, when left to cool slowly, remains fluid below that temperature, and solidifies very gradually in the amorphous state; a thermometer immersed in it during the cooling does not remain stationary at any point, or indicate any temperature at which the latent heat of the selenium is set free. Amorphous selenium retains its condition for a long time at ordinary temperatures; but between 80° and 217° C. (176° and 412·6° F.), it becomes crystalline and gives out great heat, most quickly between 125° and 180° C. (257° and 356° F.), and when pulverized. When amorphous selenium is heated in an air-bath to between 125° and 130° C., a thermometer immersed in it rises suddenly to between 210° and 215° C. Selenium, as precipitated in the red, finely divided state from selenious acid by sulphurous acid and other reducing agents, or from an aqueous solution of seleniuretted hydrogen by exposure to the air, is amorphous, and exhibits the above-mentioned spontaneous rise of temperature when heated. Selenium deposited from solutions of selenide of potassium or ammonium by exposure to the air, is crystalline, and has a sp. gr. of 4·808 at 60° F. These modifications of selenium are analogous to those of sulphur (p. 780). Berthelot finds that selenium deposited at the positive pole in the electrolysis of hydroselenic acid, is soluble in bisulphide of carbon; but that which is deposited

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* Traité de Chimie générale, par Pelouze et Fremy, 2me. edition, i. 430.

at the negative pole in the electrolysis of selenious acid is insoluble. Amorphous selenium does not conduct electricity; crystalline selenium conducts it much better, and its conducting power increases rapidly with its temperature. (Hittorff.*)

Quantitative estimation of Selenium. — The methods for the estimation and separation of selenium are similar to those which are applied to tellurium (p. 529). When in the form of selenious acid, it is precipitated in the free state by sulphurous acid. Selenic acid must first be reduced to selenious acid by heating with hydrochloric acid; it may also be precipitated as a baryta-salt, like sulphuric acid. Selenious and selenic acid may be separated from certain metals, iron, zinc, &c., by hydrosulphuric acid, which throws down sulphide of selenium; from others, such as copper, silver, and lead, by sulphide of ammonium, which dissolves sulphide of selenium. Metallic selenides may be decomposed by heating them in a current of chlorine gas, the volatile chloride of selenium being received in water, which decomposes it and precipitates the selenium.

PHOSPHORUS.

Red or amorphous Phosphorus (p. 314). — When phosphorus is subjected to the action of the sun's rays, or to a high temperature in vacuo, or in a gas which does not act upon it chemically, it quickly assumes a red colour, and becomes completely altered in its properties. This modified phosphorus may be obtained in considerable quantity by heating ordinary phosphorus to 230° — 250° C. (446°—482° F.) in a retort filled with nitrogen or carbonic acid, and having adapted to its beak a bent tube which dips under mercury. Part of the phosphorus condenses on the neck of the retort in the ordinary state, but the rest is transformed in the course of a few hours into a dark red mass, which is a mixture of amorphous and ordinary phosphorus. On treating this mixture with bisulphide of carbon, the latter is dissolved, and the amorphous phosphorus remains in the form of a red powder.

This amorphous phosphorus differs remarkably from ordinary phosphorus, both in its physical and in its chemical properties. Its sp. gr. at 10° C. (50° F.) is 1·964, while that of ordinary phosphorus is between 1·826 and 1·840; it sinks in melted phosphorus, the density of that liquid at 45° C. being 1·88. It melts at 250° C., and at 260° is reconverted into ordinary phosphorus. Red phosphorus is much less energetic in its chemical affinities than ordinary phosphorus. At ordinary temperatures it has no perceptible odour, and may be exposed to the air without alteration. It does not become luminous in the air till heated to 200° C., or take fire below 260°. It does not combine with melted sulphur. It combines with chlorine without emission of light; with bromine, however, it exhibits that phenomenon. It is insoluble in bisulphide of carbon, alcohol, ether, rock-oil, and terchloride of phosphorus. Oil of turpentine and a few other liquids dissolve small quantities of it (Schrötter†).

Amorphous phosphorus may be obtained in the compact state by keeping phosphorus for several days at a temperature a little below 260° C. It is then converted into a brittle, easily friable, reddish-brown mass, having a conchoïdal fracture, and exhibiting on the fractured surface, an iron-grey colour and imperfect metallic lustre. As thus prepared, however, it is not quite pure, but contains a small quantity of ordinary phosphorus, which causes it to oxidate at ordinary temperatures. The density of this compact red phosphorus was found to be between 2·089 and 2·106; if quite pure, it would be still denser (Schrötter‡).

Phosphorus may also be brought to the amorphous state by heating it with a small quantity of iodine. When phosphorus is melted in a glass vessel filled with

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* Pogg. Ann. lxxxiv. 214.

† Wien. Akad. Ber. 1848, 130; Ann. Ch. Phys. [3], xxiv. 406.

‡ Pogg. Ann. lxxxi. 299; Compt. rend. xxxi. 138.

carbonic acid gas, and a small quantity of iodine introduced through an upright glass tube reaching nearly to the phosphorus, a violent action takes place, attended with great rise of temperature, and a hard, black, semi-metallic mass is produced, which yields a red powder. The same result is obtained when phosphorus is melted under strong hydrochloric acid, and a small quantity of iodine added; under water the experiment does not succeed. The product thus obtained is nearly pure amorphous phosphorus, containing only a trace of iodine; when strongly heated, it distils over almost without alteration, the distillate containing only a trace of ordinary phosphorus. The mode of its formation appears to be this:—An iodide of phosphorus is first formed, probably PI_2, and the phosphorus contained in it passes into the amorphous state; this compound is then decomposed, the amorphous phosphorus separated, and a more volatile iodine compound formed, which acts upon another portion of phosphorus with the same final result, so that by repetition of these processes a large quantity of phosphorus may be brought into the amorphous state (Brodie*). Amorphous phosphorus thus prepared differs in some respects from that which is obtained by the action of heat, being more readily attacked by potash, and precipitating certain metallic solutions (*e. g.* sulphate of copper), an effect which may perhaps be due to the small quantity of iodine contained in it. The sp. gr. of this amorphous phosphorus is 2·23.

The formation of amorphous phosphorus under the influence of iodine shows that it possesses an electro-positive character, like amorphous sulphur; a conclusion which is further confirmed by its formation in a similar manner under the influence of bromine and chlorine, and by the imperfect combustion of phosphorus or phosphuretted hydrogen (Berthelot). According to Schrötter, the substance usually regarded as oxide of phosphorus, P_2O, is nothing more than amorphous phosphorus.

Atomic weight of Phosphorus.—By burning amorphous phosphorus in oxygen gas, Schrötter finds that the atomic weight of phosphorus is 31.†

Modifications of Metaphosphoric acid (p. 654).—This acid appears to be susceptible of five polymeric modifications, viz.:

Monometaphosphoric acid	$HO.PO_5$.
Dimetaphosphoric acid	$2HO.2PO_5$.
Trimetaphosphoric acid	$3HO.3PO_5$.
Tetrametaphosphoric acid	$4HO.4PO_5$.
Hexametaphosphoric acid	$6HO.6PO_5$.

The formulæ of these several modifications are deduced chiefly from the relative numbers of atoms of the two bases in the double salts which they form.

Monometaphosphoric acid is the variety discovered by Maddrell. It is produced in combination with potash, when that alkali and phosphoric acid are ignited together in equivalent proportions,—and, in combination with oxide of ammonium, by heating dimetaphosphate of ammonia to 250° C. (482° F.). It does not form any double salts, and probably therefore contains only one atom of acid and base: $MO.PO_5$.

Dimetaphosphoric acid is produced when phosphoric acid is heated with oxide of copper, zinc, or manganese in equal or nearly equal numbers of atoms. The copper-salt, which serves for the preparation of all the others, is obtained by heating to 350° C. (662° F.) a solution of phosphoric acid and oxide of copper in the proportion of $5PO_5$ to $4CuO$. It is a crystalline powder, insoluble in water, but soluble, with the aid of heat, in sulphuric acid and in ammonia. The dimetaphosphates of the alkalies, which are obtained by treating the copper-salt with sulphide of potassium, &c., are soluble in water, crystallizable, and converted by heat into insoluble salts. Dimetaphosphoric acid has a strong tendency to form

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[*] Chem. Soc. Qu. J. v. 289.

[†] Ann. Ch. Phys. [3], xxxviii. 131.

double salts, all of which contain equal numbers of atoms of the two bases; $(MO.M'O).2PO_5$; hence its composition is inferred. For example, on mixing a concentrated solution of the potash-salt with chloride of sodium, or of the soda-salt with chloride of potassium, a crystalline double salt is obtained, having the composition $(NaO.KO).2PO_5 + 2HO$; and by mixing 2 at. ditmetaphosphate of ammonia with 1 at. chloride of copper, in tolerably concentrated solutions, and adding alcohol, blue needle-shaped crystals are formed, containing $(CuO.NH_4O).2PO_5 + 4HO$.

Trimetaphosphoric acid is produced in the form of a soda-salt by slowly cooling a fused mixture of 1 at. PO_5 and 1 at. soda. Its double salts contain 2 atoms of one base to 1 atom of the other, $(2MO.M'O).3PO_5$.

Tetrametaphosphoric acid is formed by heating phosphoric acid with oxide of lead, bismuth, or cadmium, or with a mixture of equal numbers of atoms of soda and oxide of copper. The lead-salt is easily decomposed by alkaline sulphides, and yields the corresponding salts of the alkalies. The soda-salt in combination with water is viscid and elastic, and forms with a larger quantity of water a gummy mass, which will not pass through a filter. The double salts of this acid contain equal numbers of atoms of their two bases, like those of dimetaphosphoric acid; but as they differ in physical properties from those of the latter, it is probable that they are composed according to the formula $(2MO.2M'O).4PO_5$, *e.g.* the copper and sodium salt $= (2CuO.2NaO).4PO_5$.

Hexametaphosphoric acid is the first discovered modification of metaphosphoric acid (see page 321). It is formed by igniting the hydrate of phosphoric acid, by the sudden cooling of the soda-salt, and by igniting phosphoric acid with oxide of silver. It forms double salts, the quantities of base in which are nearly in the proportion of 5 at : 1 at.; hence the composition of these salts is inferred to be: $(5MO.M'O).6PO_5$; thus the soda and lime salt is $(5CaO.NaO).6PO_5$ (Fleitmann).*

Action of Water at high temperatures on the Pyrophosphates and Metaphosphates. — These salts heated with water in sealed tubes to 280° C. (536° F.), are decomposed, with formation of tribasic phosphates. If the base of the pyrophosphate forms an insoluble tribasic phosphate, the latter is precipitated, and an acid phosphate remains in solution. Thus, with pyrophosphate of silver: $2(2AgO.PO_5) + 2HO = 3AgOPO_5 + (AgO.2HO).PO_5$.

If the base of the pyrophosphate forms a soluble tribasic phosphate, the product is a neutral tribasic phosphate: thus

$$2KO.PO_5 + HO = (2KO.HO).PO_5.$$

The metaphosphates similarly treated yield insoluble phosphates and free phosphoric acid, which dissolve small quantities of the precipitated phosphates; thus with lime:

$$3(CaO.PO_5) + 6HO = 3CaO.PO_5 + 2(3HO.PO_5).$$

The metaphosphates of potash and soda yield acid phosphates:

$$NaO.PO_5 + 2HO = NaO.2HO.PO_5.†$$

Sulphides of Phosphorus. — These compounds are easily obtained by fusing sulphur with amorphous phosphorus in an atmosphere of carbonic acid; a violent action takes place, but no explosion (Kekulé).‡

Amides of Phosphoric acid. — 1. *Triphosphamide*, $N_3H_6PO_2 = N_3\left\{\begin{matrix}PO_2\\ H_3\\ H_3\end{matrix}\right.$. — When dry ammoniacal gas is slowly passed into oxychloride of phosphorus (chlo-

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* Pogg. Ann. lxxviii. 233, 238.

† A. Reynoso, Compt. rend. xxxiv. 795.

‡ Proc. Roy. Soc. vii. 38.

ride of phosphoryl, $PO_2.Cl_3$), and the product afterwards treated with water, a solution of sal-ammoniac is obtained, together with a snow-white, amorphous insoluble substance, which is triphosphamide:

$$PO_2Cl_3 + 6NH_3 = 3NH_4Cl + N_3H_6PO_2.$$

This compound is scarcely attacked by continued boiling with water, potash-ley, or dilute acids. It is very slowly decomposed by boiling with strong nitric or hydrochloric acid, more readily by aqua-regia. Strong sulphuric or nitro-sulphuric acid dissolves it easily at a gentle heat, forming a solution which contains ammonia and phosphoric acid. It is not completely decomposed by heating with soda-lime. When fused with hydrate of potash, it gives off a large quantity of ammonia, and leaves phosphate of potash. Heated alone, out of contact of air, it also gives off ammonia, and leaves monophosphamide, which, on being heated with potash, evolves more ammonia, and leaves phosphate of potash. The compound may be regarded as tribasic phosphate of ammonia *minus* 6 at. water: —

$$\left.\begin{matrix}PO_2\\(NH_4)_3\end{matrix}\right\}O_6 - 6HO = N_3\left\{\begin{matrix}PO_2\\H_6\end{matrix}\right.$$

By the action of anhydrous aniline, $N . \overbrace{(C_{12}H_5) . H . H}$, on oxychloride of phosphorus, the homologous compound *triphenylphosphamide*, $N_3.\overbrace{PO_2.(C_{12}H_5)_3.H_3}$, is obtained; it is a white mass, more easily decomposable than triphosphamide. *Trinaphtylphosphamide*, $N.\overbrace{PO_2.(C_{20}H_7)_3.H_3}$, is obtained in like manner by the action of naphtylamine, $N . \overbrace{(C_{20}H_7) . H . H}$, on oxychloride of phosphorus.

Sulphotriphosphamide, $N_3.\overbrace{PS_2.H_3}.H_3$, is obtained by treating sulphochloride of phosphorus, PS_2Cl_3, with ammoniacal gas; it is also a white mass, which is decomposed by water, with evolution of hydrosulphuric acid gas. *Sulphotriphenylphosphamide*, $N_3 . \overbrace{PS_2 . (C_{12}H_5)_3}H_3$, is obtained in like manner, by the action of aniline on sulphochloride of phosphorus. (Hugo Schiff).*

2. *Biphosphamide*, $N_2H_3PO_2 = N_2 . \overbrace{PO_2 . H_3}$. (*Gerhardt's Phosphamide*)†.— Obtained by saturating pentachloride of phosphorus with ammoniacal gas, and then boiling with water. Chlorophosphamide, $N_2H_4PCl_3$, appears to be first formed, and afterwards resolved by water into hydrochloric acid and biphosphamide:

$$PCl_5 + 2NH_3 = N_2H_4PCl_3 + 2HCl;$$

and—

$$N_2H_4PCl_3 + 2HO = N_2H_3PO_2 + 3HCl.$$

The product is purified by boiling, first with caustic potash, then with nitric or sulphuric acid, and, finally, by washing water. It is a white powder, insoluble in water, alcohol, and oil of turpentine. When heated without access of air, it gives off ammonia, and leaves monophosphamide; but if moisture be present, it yields ammonia and metaphosphoric acid. Fused with hydrate of potash, it gives off ammonia and leaves phosphate of potash. It resists the action of most oxidizing agents; but is slowly oxidized by fusion with nitre, and deflagrates with chlorate of potash. It may be regarded as bi-ammoniacal phosphate of ammonia (the so-called neutral phosphate,) *minus* 6HO: —

$$\left.\begin{matrix}PO_2\\(NH_4)_2.H\end{matrix}\right\}O_6 - 6HO = N_2\left\{\begin{matrix}PO_2\\H_3\end{matrix}\right.$$

Liebig and Wöhler, who discovered this compound, supposed it to be a bihydrate of phosphide of nitrogen, $PN_2.2HO$.

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* Ann. Ch. Pharm. ci. 300.

† Ann. Ch. Phys. [3], xviii. 188.

3. *Monophosphamide*, $N.PO_2$. (*Gerhardt's Biphosphamide*).—Obtained by heating triphosphamide or biphosphamide, without access of air:—

$$N_3H_6PO_2 - 2NH_3 = N.PO_2,$$

and:

$$N_2H_3PO_3 - NH_3 = N.PO_2.$$

It is a pulverulent substance, resembling triphosphamide in its reactions, but still more difficult to decompose (Gerhardt, Schiff). It may be regarded as ammonia, NH_3, in which the 3 at. hydrogen are replaced by the tribasic radical, PO_2, or as mono-ammoniacal phosphate of ammonia (the so-called acid phosphate), *minus* 6HO:—

$$\left.\begin{matrix}PO_2\\(NH_4).H_2\end{matrix}\right\}O_6 - 6HO = NPO_2.$$

4. *Phosphamic acid*, $NH_2PO_4 = \left.\begin{matrix}\overbrace{N.H.PO_2}\\H\end{matrix}\right\}O_2$.—This compound, which may be regarded as hydrated oxide of ammonium, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}O_2$ in which 3 at. hydrogen in the ammonium are replaced by PO_2, is obtained by the action of ammoniacal gas on anhydrous phosphoric acid:—

$$\left.\begin{matrix}PO^2\\PO_2\end{matrix}\right\}O_6 + 2NH_3 = 2\left.\begin{matrix}\overbrace{N.H.PO_2}\\H\end{matrix}\right\}O_2 + 2HO.$$

Great heat is evolved, and the product, when cold, is a fused mass, consisting of phosphamic acid and phosphamate of ammonia, generally mixed with red phosphorus. On dissolving this mass in water, and filtering, a solution is obtained, from which the other salts, most of which are insoluble, may be formed by double decomposition. The free acid, which may be obtained by decomposing the lime-salt with sulphuric acid, is a semi-solid, amorphous mass, which dissolves easily in water and alcohol, and when heated, gives off ammonia, and leaves phosphoric acid.

The phosphamates of the earths, and heavy metals, are insoluble in water, and very sparingly soluble in acids, a character which distinguishes them from the phosphates. The ammonia-salt gives white precipitates with salts of barium, strontium, calcium, magnesium, iron, manganese, zinc, lead, mercury, and silver, rose-coloured with cobalt, greenish-white with nickel, light-blue with copper, and dirty green with chromium salts. The iron salt, $NHFePO_4$, dissolves in ammonia, forming a deep purple solution, which on evaporation leaves a crystalline salt, the *phosphamate of ferrammonium*, $\left.\begin{matrix}NH.PO_2\\NH_3Fe\end{matrix}\right\}O_2$. The phosphamates of cobalt, nickel, zinc, copper, mercury and silver likewise dissolve in ammonia, apparently with formation of analogous salts. (Schiff.)*

5. *Phospham*, $N_2P.H$.—When anhydrous phosphoric acid, saturated as completely as possible with ammoniacal gas, is heated in a dry current of that gas, it is decomposed, and on treating the mass when cold with water, phosphoric acid dissolves, and there remains a small quantity of a yellowish red residue, which gives off ammonia when fused with potash, and exhibits in other respects, the characters of phospham (Liebig and Wöhler's phosphide of nitrogen, p. 328). This compound is the nitrile of phosphamic acid, being related to it in the same manner as aceto-nitrile, $N.C_4H_3$, to acetic acid (Schiff):—

$$NH\,(NH_4)\,PO_4 - 4HO = N_2PH.$$

Gladstone,† by the action of alkalies on chlorophosphide of nitrogen (p. 796), obtained two acids, *azophosphoric* and *deutazophosphoric* acids, which he regarded

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* Ann. Ch. Pharm. ciii. 168.

† Chem. Soc. Qu. J. iii. 135, 353.

as phosphoric acid conjugated with one and two atoms of the group PN. Thus phosphoric acid, $= PO_5$; azophosphoric acid, $= PN.PO_5$; deutazophosphoric acid, $= (PN)_2.PO_5$. These acids, according to Gladstone's analyses, are both tribasic, the formula of the azophosphates being $3MO.P_2NO_5 = P_2NM_3O_8$; and that of the deutazophosphates, $3MO.P_3N_2O_5 = P_3N_2M_3O_8$. It is probable, however, that deutazophosphoric acid is the same as Schiff's phosphamic acid.

The formation of deutazophosphoric acid from chlorophosphide of nitrogen ($N_2P_3Cl_5$), is represented, according to Gladstone, by the equation —

$$N_2P_3Cl_5 + 5HO = 5HCl + P_3N_2O_5.$$

Laurent, however, has shown that the formula of chlorophosphide of nitrogen is more probably $NPCl_2$; and from this it is easy to deduce the formation of phosphamic acid:—

$$NPCl_2 + 4HO = 2HCl + NH_2PO_4.$$

Moreover the analysis of the deutazophosphates of baryta and silver agree with the formulæ of the phosphamates $NHMPO_4$ quite as well as with Gladstone's formula. By decomposing chlorophosphide of nitrogen with ammonia, Gladstone obtained in three experiments, 181, 183, and 177 per cent. of an ammoniacal salt. Regarding this as phosphamate of ammonia, and representing its formation by the equation —

$$NPCl_2 + 3\left.\begin{matrix}NH_4\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}NHPO_2\\NH_4\end{matrix}\right\}O_2 + 2NH_4Cl + 2HO,$$

the quantity should be 175 per cent., which agrees nearly with the experimental result.

Azophosphoric acid, which appears to be a product of the decomposition of deutazophosphoric acid, is most probably *pyrophosphamic acid*, $\left.\begin{matrix}N_3\overbrace{H_8.P_2}O_6\\H_3\end{matrix}\right\}O_6$, the tribasic amidogen acid of quadribasic pyrophosphoric acid, $P_2H_4O_{14}$.

Quantitative estimation of Phosphorus and its compounds.—Phosphorus is always estimated in the form of phosphoric acid. When it occurs in combination with a metal, or in an organic compound, or as phosphorous or hypophosphorous acid, it is brought to the highest state of oxidation by treatment with nitric acid, aqua-regia, or a mixture of hydrochloric acid and chlorate of potash.

The precipitation of phosphoric acid (tribasic) from an aqueous solution, in which it exists in the free state or combined with an alkali, is best effected by the addition of sulphate of magnesia and excess of ammonia, chloride of ammonium being likewise added to prevent the precipitation of magnesia in the form of hydrate. The phosphoric acid is then precipitated as phosphate of magnesia and ammonia, $NH_4O.2MgO.PO_5$. The precipitate does not settle down at once, but its deposition may be accelerated by leaving the vessel in a warm place. Care must be taken, however, not to allow the liquid to become very hot, as in that case hydrate of magnesia will be precipitated, and will be very difficult to redissolve. The precipitate, after standing for about two hours, is collected on a filter and washed with water containing ammonia, as pure water decomposes it. It is then dried and ignited, whereby it is converted into pyrophosphate of magnesia, $2MgO.PO_5$, containing 63·67 per cent. of phosphoric acid, PO_5, and 27·98 per cent. of phosphorus.

If the phosphoric acid is in the monobasic or bibasic modification, it must first be converted into the tribasic acid by fusing the salt with five or six times its weight of carbonate of soda, or, better, with a mixture of carbonate of potash and carbonate of soda in equivalent proportions. The mixture may then be fused over a lamp, whereas if carbonate of soda or carbonate of potash alone be used, the heat of a furnace will be required. By this fusion with excess of an alkaline carbonate, the phosphoric acid is in most cases completely separated from any other base with which it may be combined, and converted into a tribasic phosphate of the alkali, which may then be treated as above.

Phosphates which are insoluble in water, may be dissolved in nitric or hydrochloric acid; and from these solutions, the bases may in some cases be precipitated by hydrosulphuric acid, in others by sulphide of ammonium, and the phosphoric acid subsequently precipitated from the filtered solution in the form of the ammonio-magnesian phosphate in the manner above described.

To separate phosphoric acid from the *earths*, other methods are required. From *baryta* it is easily separated by sulphuric acid, which throws down the baryta; from *strontia* and *lime*, also, by sulphuric acid with addition of alcohol. From *magnesia* it may be separated by fusion with a mixture of carbonate of potash and carbonate of soda in equivalent proportions. From *alumina* it is most readily separated by dissolving the compound in hydrochloric acid, adding sufficient tartaric acid to keep the alumina in solution when the liquid is neutralized by an alkali, and then adding excess of ammonia and sulphate of magnesia, whereby a precipitate of ammonio-magnesian phosphate is produced, which may be treated as already described. This method may also be applied to the separation of phosphoric acid from iron.

When phosphoric acid exists in combination with several earthy bases together, it may be separated by dissolving the compound in nitric acid, adding metallic mercury in slight excess, evaporating over the water-bath to perfect dryness, and treating the residue with water. The whole of the phosphoric acid then remains undissolved in the form of mercurous phosphate, while the bases pass into the solution as nitrates. (H. Rose). This method, however, requires attention to a number of details and precautions which cannot here be given.

Another method of separating phosphoric acid from a mixture of bases, by means of acetate of uranium, has already been described (p. 557).

The salts of phosphorous and hypophosphorous acid may be oxidized by nitric acid, the former being thereby converted into pyrophosphates, the latter into metaphosphates. These salts must then be converted into tribasic phosphates in the manner above described.

Phosphorous and hypophosphorous acid may also be estimated by their power of precipitating gold in the metallic state from its solutions, or, better, by their reducing action on mercuric chloride, which, when present in excess, is reduced to mercurous chloride.

CHLORINE.

Chloride of Nitrogen (p. 345).—According to Bineau,[*] this compound is NCl_3, that is to say, ammonia in which all the hydrogen is replaced by chlorine Bineau's analysis gives 10·6 p.c. N, and 89·3 Cl; the formula requires 11·65 N, and 88·35 Cl. According to Porrett, Wilson, and Kirk,[†] it is $NHCl_3$; according to Gladstone,[‡] N_2HCl_5, or $NHCl_2 + NCl_3$.

Sulphite of Perchloride of Carbon, $C_2Cl_4 . 2SO_2$.— This body was discovered by Berzelius and Marcet, who obtained it by the action of aqua-regia on bisulphide of carbon; but a better mode of obtaining it is the following: — A bottle, capable of holding about three pints, is half filled with a mixture of peroxide of manganese and hydrochloric acid; about 800 grains of bisulphide of carbon are then added; the vessel quickly closed, and left for some days in a cool place. It is then exposed for several days longer to a temperature of 30° C. (86° F.), or in summer to direct sunshine, and frequently shaken, till the greater part of the bisulphide of carbon is converted into the new compound. The action may be

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[*] Ann. Ch. Phys. [3], xv. 71.

[†] Gmelin's Handbook, ii. 472.

[‡] Chem. Soc. Qu. J., vii. 51.

greatly accelerated by adding a quantity of nitric acid equal in weight to twice that of the bisulphide of carbon used. The mixture is then distilled, whereupon undecomposed bisulphide of carbon first passes over, together with chloride of sulphur and a peculiar yellow liquid ($C_4S_4Cl_4$), and afterwards the sulphite of perchloride of carbon condenses in the solid form in the neck of the retort. The formation of this compound is represented by the following equation:—

$$2CS_2 + 8Cl + 4HO = C_2Cl_4 . 2SO_2 + 4HCl + 2S.$$

Sulphite of perchloride of carbon is a white crystalline solid having a highly pungent odour, and exciting tears. It melts at 135° C. and boils at 170°; may be sublimed, and forms small rhombohedral crystals, It is soluble in alcohol, ether, and bisulphide of carbon; insoluble in water. It is decomposed at a dull red heat, yielding chlorine, sulphurous acid, and protochloride of carbon:—

$$2(C_2Cl_4 . 2SO_2) = 4Cl + 4SO_2 + 2C_2Cl_2.$$

It decomposes slowly in contact with water or moist air, yielding sulphurous, sulphuric, carbonic, and hydrochloric acids. Heated with a large excess of strong sulphuric acid, it gives off sulphurous acid, anhydrous sulphuric acid, hydrochloric acid, and phosgene gas:—

$$C_2Cl_4 . 2SO_2 + 2SO_4H = 2SO_2 + 2SO_3 + 2HCl + 2COCl.^*$$

Chlorosulphide of Carbon, $C_4S_4Cl_4$.—The liquid distillate obtained in the preparation of the preceding compound contains this substance, which may be obtained from it in a state of purity by repeated distillation with water and hydrate of magnesia, which decomposes the chloride of sulphur. It may also be prepared by exposing bisulphide of carbon to sunshine in an atmosphere of dry chlorine—

$$CS_2 + 2Cl = SCl + CSCl,$$

and purified as above. Also by passing a mixture of hydrosulphuric acid gas and vapour of perchloride of carbon through a red-hot tube:—

$$2C_2Cl_4 + 4HS = 4HCl + C_4S_4Cl_4.$$

It is a yellow liquid, not miscible with water; has a peculiar and powerful odour, and irritates the eyes very strongly; Sp. gr. 1·46. It boils at 70° C. (158° F.) It is not decomposed by water or acids, not even by nitric acid. Bisulphide of carbon and caustic potash decompose it gradually. It absorbs ammoniacal gas (Kolbe†).

Sulphite of Protochloride of Carbon, $C_2Cl_2 . 2SO_2$.—Formed by the action of reducing agents, viz., sulphurous acid, hydro-sulphuric acid, zinc, iron, protochloride of tin, &c., on the sulphite of perchloride of carbon. It has not been obtained in the anhydrous state. It dissolves in water and alcohol, and is best prepared in the state of solution, by passing sulphurous acid gas through an alcoholic solution of sulphite of perchloride of carbon. The solution is colourless and inodorous, has an acid reaction, and absorbs oxygen rapidly, forming sulphuric acid and phosgene:—

$$C_2Cl_2.2SO_2 + 4O = 2SO_3 + 2COCl.$$

Chlorine converts it into $C_2Cl_4.2SO_2$. (Kolbe).

Perchlorocarbosulphurous acid, $C_2Cl_3O.2SO_2.HO$.—Formed by the action of caustic alkalies on sulphite of perchloride of carbon:—

$$C_2Cl_4.2SO_2 + 2KO = C_2Cl_3O.2SO_2.KO + KCl.$$

The hydrated acid is obtained by decomposing the baryta-salt with sulphuric acid. It crystallizes in small deliquescent prisms, which may be partially sublimed without decomposition. They contain 2 at. water of crystallization, their formula

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[*] Kolbe, Ann. Ch. Pharm. liv. 148.

[†] Ibid. xlv. 53.

being $C_2Cl_3O.2SO_2.HO + 2HO$. The acid is not decomposed by fuming nitric acid or aqua-regia, and is so powerful an acid that it expels hydrochloric acid from its combinations. Its salts are all soluble in water and alcohol, and crystallize with facility. When heated they are resolved into phosgene, sulphurous acid, and a metallic chloride; *e. g.*

$$C_2Cl_3O.2SO_3.KO = 2COCl + 2SO_2 + KCl.$$

Chlorocarbosulphurous acid, $C_2Cl_2.2SO_2.2HO$.—Formed by the action of alkalies on sulphite of protochloride of carbon, or by the action of zinc on the preceding acid. Resembles the preceding in most of its properties. Its salts, when heated, give off phosgene, sulphurous acid, and water, and leave a residue of metallic chloride and charcoal.

Chloromethylosulphurous acid, $C_2HCl.2SO_2.2HO$. — Formed by the continued action of nascent hydrogen on chlorocarbosulphurous acid:—

$$C_2Cl_2.2SO_2.2HO + H = C_2HCl.2SO_2.2HO + HCl.$$

When zinc is immersed in an aqueous solution of chlorocarbosulphurous acid, it dissolves with evolution of hydrogen; and the hydrogen, as it is set free, converts part of the acid into chloromethylosulphurous acid; but complete transformation can only be obtained by subjecting an acidulated solution of a perchlorocarbosulphite or chlorocarbosulphite to the action of the galvanic current. The hydrated acid is a viscid, strongly acid liquid, which bears a heat of 140° C. without decomposition; at —16·6° C. it becomes syrupy; in other respects it resembles perchlorocarbosulphurous acid. All its salts are soluble in water, and crystallizable.

Methylosulphurous acid, $C_2H_3O.2SO_2.HO$. — Formed when a neutral solution of perchlorocarbosulphite of potash is decomposed by the electric current, the electrodes being formed of amalgamated zinc plates:—

$$C_2Cl_3O.2SO_2.KO + 6Zn + 6HO = C_2H_3O.2SO_2.KO + 6ZnO + 3HCl.$$

Also when an amalgam of potassium is immersed in the same solution,

$$C_2Cl_3O.2SO_2.KO + 6K + 3HO = C_2H_3O.2SO_2.KO + 3KCl + 3KO.$$

The concentrated solution of the hydrated acid is a sour, inodorous, viscid liquid, which may be heated to nearly 130° C. without decomposition, but at that temperature begins to turn brown and decompose. It does not crystallize when pure. It is equal to perchlorocarbosulphurous acid in stability and in affinity for bases. Its salts are soluble and crystallizable. (Kolbe*).

Intermediate Chloride of Sulphur, S_4Cl_3. — Protochloride of sulphur is readily decomposed by heat, its boiling point rising quickly from 64° to 78° C., where it remains stationary. The deep orange-yellow liquid thus obtained appears to be composed of $S_4Cl_3 = S_2Cl + 2SCl$.

Terchloride of Sulphur, SCl_3. — Not known in the separate state, but exists in the compound, $SCl_3.5SO_3$, obtained by mixing the protochloride of sulphur, SCl, with Nordhausen sulphuric acid, and distilling. Sulphurous acid and anhydrous sulphuric acid pass over first, then the compound $SCl_3.5SO_3$, while monohydrated sulphuric acid remains in the retort. The compound $SCl_3.5SO_3$ is a colourless oily liquid having a peculiar odour, and fuming slightly in the air, Its density is 1·818, and that of its vapour 4·481. Boils at 145° C. (283° F.). Water decomposes it rapidly, forming sulphuric and hydrochloric acids. (H. Rose.)

Chlorosulphuric acid, SO_2Cl, is regarded by some chemists as a bisulphate of terchloride of sulphur, $SCl_3.2SO_3$.†

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* Ann. Ch. Pharm. liv. 143.

† See page 301, line 25, where, however, there is a misprint, the formula being given as $3SO_3.SCl_3$ instead of $2SO_3.SCl_3$.

Sulphate of Bichloride of Sulphur, $SCl_2.SO_3 = S_2Cl_2O_3$.—Formed by the action of moist chlorine gas on protochloride of sulphur. Large transparent colourless crystals, which are decomposed by alcohol and water, or even by exposure to damp air. Enclosed in a sealed glass tube, they change in the course of a few months into a very mobile, slightly yellow liquid, which has the same composition as the crystals, but does not solidify at — 18° C. (0° F.). It is dissolved by water, with formation of sulphuric and hydrochloric acids. The compound $S_2Cl_2O_3$ may be regarded as hyposulphuric acid in which 2 at. O are replaced by chlorine. (Millon.*)

Chlorosulphide of Phosphorus, $PS_{10}Cl_4$. —Besides the chlorosulphide of phosphorus described on page 349, another compound of these elements, having the formula just given, is obtained by passing a stream of phosphuretted hydrogen into dichloride of sulphur. This compound is a yellow syrupy liquid, which is decomposed by water, with evolution of hydrosulphuric acid and deposition of sulphur. It may be regarded as a compound of dichloride of sulphur with a peculiar sulphide of phosphorus, not yet isolated:—

$$4S_2Cl + PS_2 = PS_{10}Cl_4.$$

This compound was discovered by H. Rose.

Sulphide of Pentachloride of Phosphorus, $PCl_5.S_4$.—When a mixture of 3 pts. pentachloride of phosphorus and 1 pt. of sulphur is melted, a colourless liquid is obtained, which boils at about 100° C. It dissolves large quantities of pentachloride of phosphorus and sulphur, the latter of which it deposits in crystals; it is very difficult to purify. Water decomposes it immediately, with formation of a great number of products (Gladstone.)† The compound may be regarded as $PS_2Cl_3 + Cl_2S_2$ (Schiff‡).

Action of acids on Pentachloride of Phosphorus. — Persoz and Bloch,§ by passing dry sulphurous acid gas over pentachloride of phosphorus, obtained a volatile, strongly refracting liquid which they regarded as $PCl_5.2SO_2$. According to Schiff‖, however, this liquid is decomposed by fractional distillation, being resolved into oxychloride of phosphorus which boils at 110° C. (230 F.), and a more volatile liquid, which passes over at 82° C. (147·6 F.). This latter is the *chloride of thionyl*, $S_2O_2.Cl_2$, the name thionyl denoting the biatomic radical, S_2O_2, of sulphurous acid and its salts, hydrated sulphurous acid being $\left.\begin{matrix}S_2O_2\\H_2\end{matrix}\right\}O_4$, and anhydrous sulphurous acid, $S_2O_2.O_2$. Chloride of thionyl is a volatile liquid of great refracting power, and having a suffocating odour like that of sulphurous acid. It is decomposed by water, and more readily by alkalies, into hydrochloric and sulphurous acids. With alcohol, it yields hydrochloric and ethylosulphurous acids.

Thionamide, $N_2\left\{\begin{matrix}S_2O_2\\H_4\end{matrix}\right.$, is produced when chloride of thionyl is brought in contact with dry ammonia:

$$S_2O_2 . Cl_2 + 4NH_3 = 2NH_4Cl + N_2(S_2O_2)H_4.$$

The action is very violent, but may be moderated by cooling. The product is a white, non-crystalline solid, which gives up sal-ammoniac when digested in water, and is afterwards completely decomposed.

Anhydrous sulphuric acid acts upon pentachloride of phosphorus in the same manner as anhydrous sulphurous acid, producing a liquid which Persoz and Bloch regarded as $PCl_5 . 2SO_3$, but which, according to Schiff, is resolved by distillation

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* Ann. Ch. Pharm. lii. 230; lxxvi. 235.

† Chem. Soc. Qu. J. iii. 5.

‡ Ann. Ch. Pharm. ci. 309.

§ Compt. rend. xxvii. 86.

‖ Ann. Ch. Pharm. cii. 111.

into oxychloride of phosphorus, and chloride of sulphuryl or chlorosulphuric acid, $S_2O_4 . Cl_2$.

With *hydrated sulphuric acid,* pentachloride of phosphorus forms *chlorohydrated sulphuric acid,* S_2HClO_6:

$$\left.\begin{matrix}S_2O_4\\H_2\end{matrix}\right\}O_4 + PCl_5 = \left.\begin{matrix}S_2O_4\\HCl\end{matrix}\right\}O_2 + HCl + PO_2Cl_3.$$

And this compound, by the further action of the pentachloride, is converted into chlorosulphuric acid, $S_2O_4 . Cl_2$ (p. 709). Chlorohydrated sulphuric acid is a liquid which boils at 145° C., is decomposed by water, yielding hydrochloric and sulphuric acids, and dissolves chloride of sodium at a gentle heat, with evolution of hydrochloric acid and formation of the compound S_2NaClO_6. It effervesces with melted nitre, giving off a vapour (probably NO_4Cl) which smells like aqua-regia, and when passed into water, forms nitric and hydrochloric acids. The compound S_2HClO_6 is probably identical with that which H. Rose obtained by the action of sulphuric acid on pentachloride of sulphur, and regarded as S_2O_5Cl. It is likewise obtained in small quantity by the action of strongly heated platinum-black on an imperfectly dried mixture of chlorine and sulphurous acid. (Williamson*).

Tungstic acid treated with pentachloride of phosphorus yields oxychloride of phosphorus and an oxychloride of tungsten, $W_2O_4Cl_2$. Similarly with molybdic acid.

Hydrated antimonic acid heated with pentachloride of phosphorus yields hydrochloric acid and oxychloride of phosphorus, with a residue of anhydrous antimonic acid.

Anhydrous phosphoric acid and pentachloride of phosphorus form oxychloride of phosphorus:

$$P_2O_{10} + 3PCl_5 = 5PO_2Cl_3.$$

When strong *nitric acid* is cautiously added to pentachloride of phosphorus, hydrochloric acid is evolved; and if the escaping vapour be passed through a good refrigerating apparatus, a blood-red liquid condenses, which when distilled yields yellowish-red vapours, probably NO_4Cl, and distillate of oxychloride of phosphorus. (Schiff).

Chlorophosphide of Nitrogen, $P_2N_2Cl_5$ according to Wöhler and Liebig, who discovered it; $P_3N_2Cl_3$ according to Gladstone; $PNCl_2$ according to Laurent. It is formed by the action of ammonia on pentachloride of phosphorus. On treating the crude product with ether, the chlorophosphide of nitrogen is alone dissolved, and may then be crystallized. It is also produced by distilling a mixture of 1 pt. pentachloride of phosphorus with 2 pts. sal-ammoniac. It may be purified by distillation with water, being carried over by the vapour of water, and then only requires to be dried. It crystallizes in rhomboidal prisms; melts at 110°, and boils at 240° C. It is insoluble in water, but dissolves in alcohol, ether, and oil of turpentine. Alkalies decompose it, with formation of phosphamic acid (p. 790).

BROMINE.

Bromine of Nitrogen.—When chloride of nitrogen is gently heated with bromide of potassium, double decomposition takes place, and a brown, very heavy, oily liquid is formed, which appears to be bromide of nitrogen. It is very volatile, has an offensive odour, and irritates the eyes strongly. It detonates easily, and is decomposed by hydrochloric acid, hydrobromic acid, and ammonia. Its composition appears to be NBr_3. (Millon).

Oxybromide of Phosphorus, PBr_3O_2.—Produced by the decomposition of the

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* Proceedings of the Royal Society, vii. 11.

pentabromide in moist air. When the thick reddish liquid thus formed is heated, to drive off the hydrobromic acid which it contains, and then distilled at about 180° C. (366° F.), the oxybromide passes over in the form of a colourless heavy liquid, which boils between 170° and 200° C. It does not mix with water, but is slowly decomposed by that liquid, with formation of phosphoric and hydrobromic acids. It dissolves in oil of turpentine, ether, and strong sulphuric acid, and is precipitated from the last-mentioned solution by water. Nitric acid decomposes it, with evolution of bromine. Another body, apparently of the same composition, but solid and crystalline, is sometimes obtained as a residue in the distillation of pentabromide or oxybromide of phosphorus, and by the action of moist air on the pentabromide in an imperfectly-closed vessel. It is decomposed by water, melts and volatilizes when heated, but on cooling remains as a liquid, exhibiting the characters of the oxybromide. (Gladstone*).

Sulphobromide of Phosphorus.—Pentabromide of phosphorus is decomposed by hydrosulphuric acid, with formation of a heavy liquid, which boils without decomposition at 200° C., and appears to have the composition $3PBr_3 . PS_3$; it may, however, be a mixture of two compounds having nearly the same boiling point. (Gladstone†).

IODINE.

Natural sources of Iodine.—According to Chatin,‡ iodine exists in the air, in nearly all water, and in a great number of plants, land and fresh-water as well as marine; also in coal, in various chemical products, viz., commercial potash, soda, and sal-ammoniac, in wine, cider, perry, &c., in milk and eggs. He finds also that iodine is least abundant in the air and water of those localities in which goitre and cretinism prevail. Similar results have been obtained by other chemists. On the other hand, Macadam,§ Lomeyer,‖ and others have not been able to detect iodine in the air or in rain-water. Macadam, however, found iodine in commercial potash, in numerous samples of alkaline carbonates (used as reagents), in the ashes of wood-charcoal, in coal, and in numerous plants. Lomeyer examined particularly the air and water of various localities where goitre is scarce, but found no trace of iodine. Chatin ¶ attributes the negative results obtained by Macadam and Lomeyer to defective methods of analysis, but does not give any exact description of his own process.

Hypoiodic acid, IO_4, *and Sub-hypoiodic acid*, $I_5O_{19} = 4IO_3 + IO_7$. — When one part of iodic acid and 5 parts of monohydrated sulphuric acid are heated in a platinum crucible, till oxygen gas and afterwards vapours of iodine are evolved, a green solution is obtained; and on leaving this for some days in a dry atmosphere, a yellow crystalline crust is deposited, which, when freed from the excess of sulphuric acid and washed with water and alcohol, yields sub-hypoiodic acid; and this compound heated to 150° C. gives off vapour of iodine, and is converted into hypoiodic acid. The latter is a sulphur-yellow amorphous powder, which at 180° C. is resolved into iodic acid and iodine. Water and nitric acid decompose it in a similar manner. Sulphuric acid dissolves it with the aid of heat, and on cooling deposits a compound consisting of $IO_4 . 4SHO_4$. Aqueous alkalies decompose hypoiodic acid, forming iodates and the other compounds which result from the action of iodine on alkalies.

Sub-hypoiodic acid bears a considerable resemblance to hypoiodic acid, both in physical and chemical properties. When heated, it gives off iodine and leaves hypoiodic acid. (Millon.)

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* Phil. Mag. [3], xxxv. 345.

† Ibid.

‡ Compt. rend. xxx. 352; xxxi. 280; xxxii. 669; xxxiii. 519, 529, 581.

§ Chem. Soc. Qu. J., vi. 166.

‖ Phil. Mag. [4], vii. 237.

¶ J. Pharm. [3], xxv. 192.

Iodide of Nitrogen (p. 358).—Gladstone* has analyzed this compound (as prepared by precipitating an alcoholic solution of iodine with excess of ammonia and washing with water), and arrived at results which accord with Bineau's formula, NHI_2. By decomposing the compound with hydrosulphuric acid, he finds that it contains 2I to 1N, while its decomposition by aqueous sulphurous acid agrees with the equation—

$$NHI_2 + 4SO_2 + 4HO = NH_3 + 2HI + 4SO_3.$$

Gladstone suggests for the compound the name *iodimide.* He also finds the above formula to be in accordance with the formation of the compound by the action of hypochlorite of lime on iodide of ammonium (observed by Playfair), that reaction being attended with evolution of ammonia, according to the equation—

$$2(CaO.ClO) + 2NH_4I = NHI_2 + 2CaCl + 4HO + NH_3.$$

Bunsen takes a different view of the constitution of iodide of nitrogen. He observes: 1. That the mode of formation of this compound from iodine and ammonia, with hydriodic acid as the only secondary product, shows that it must be a substitution-product of ammonia, of the form NI_3, NHI_2 or NH_2I, associated at most with ammonia or hydriodic acid; 2. That it cannot contain hydriodic acid, because it dissolves in hydrochloric acid without evolution of gas, and forms a solution containing ammonia and protochloride of iodine, but no hydriodic acid; 3. That, to determine its composition, it is sufficient to ascertain how much ICl and how much NH_3 it yields with hydrochloric acid, and to see which of the following equations agrees with the results:—

$$(a)\ NI_3 + 3HCl = 3ICl + NH_3.$$
$$(b)\ NHI_2 + 2HCl = 2ICl + NH_3.$$
$$(c)\ NH_2I + HCl = ICl + NH_3.$$
$$(d)\ NH_2I + NH_3 + HCl = ICl + 2NH_3, \&c.$$

Preparations obtained by mixing cold and more or less saturated anhydrous alcoholic solutions of iodine and ammonia, which were not decomposed by washing with absolute alcohol, gave, when dissolved in hydrochloric acid, quantities of ammonia, iodine, and chlorine, in the atomic proportion of 2 : 3 : 3, showing that the constitution of the compound is $NI_3 + NH_3$. A preparation obtained by adding ammonia to a solution of iodine in aqua-regia diluted with water, and washed as quickly as possible with cold water, gave, with hydrochloric acid, quantities of ammonia and protochloride of iodine in the atomic proportion of 5 : 12, showing that its formula was $4NI_3 + NH_3$. When washed with water for any length of time, even till the greater part of the compound was decomposed, with separation of iodine and nitrogen, the undecomposed portion still yielded more than 1 at. ammonia to 3 at. chloride of iodine, a proof that ammonia enters essentially into its constitution. Bunsen is of opinion that there exist two distinct compounds, $NI_3.NH_3$ and $4NI_3.NH_3$, formed in the manner shown by the equations—

$$2NH_3 + 6I = (NI_3.NH_3) + 3HI;$$
$$4(NI_3.NH_3) + 3HO = 4NI_3.NH_3 + 3NH_4O.$$

The formation of the so-called iodide of nitrogen by the action of ammonia on a solution of iodine in aqua-regia, would be inconsistent with this view, if that solution contained, not ICl, but, as is commonly supposed, ICl_3, because NI_3 could not be formed by the action of ammonia upon the latter. Experiment, however, shows that the solution of iodine in aqua-regia contains only ICl. The formation of the so-called iodide of nitrogen from ICl is explained by the equation—

$$2NH_3 + 3ICl = (NI_3.NH_3) + 3HCl.$$

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* Chem. Soc. Qu. J. v. 34.

The immediate products of its explosion are nitrogen and hydriodic acid:

$$NI_3.NH_3 = 2N + 3HI,$$

which latter is for the most part resolved by the high temperature into iodine and hydrogen, while another portion unites with the ammonia of the compound, forming iodide of ammonium, thereby setting free quantities of iodine and nitrogen equivalent to this ammonia.*

Gladstone, in a subsequent communication,† remarks that his mode of preparing the iodide of nitrogen differs essentially from that of Bunsen, and that his formula NHI_2 may be written $2NI_3 + NH_3$, which shows it to be intermediate between the two formulæ given by Bunsen. He concludes, from further experiments, that the formula NHI_2 is true, not only for the preparation obtained by the method described in his former paper, but likewise for that obtained by precipitation from solutions of iodine and ammonia in absolute alcohol.

Iodides of Phosphorus (p. 358). — These compounds are best prepared by dissolving iodine and phosphorus together in bisulphide of carbon, and cooling the solution till it crystallizes. There appear to be only two iodides of phosphorus, viz. PI_2 and PI_3, which are prepared by dissolving the two substances as above, in the respective atomic proportions; if they be mixed in any other proportions, the same compounds crystallize out, together with the excess of iodine or phosphorus.

The *biniodide*, PI_2, is a light-red solid body, which melts at 110° C., forming a red liquid. Water decomposes it, with formation of hydriodic and phosphorous acid, and deposition of yellow flakes. When melted with excess of phosphorus and decomposed by water, it yields red phosphorus. It dissolves in bisulphide of carbon, and is deposited from the solution in flattened prismatic crystals, of a light-orange colour.

The *teriodide*, PI_3, forms dark-red six sided laminæ, which dissolve very readily in bisulphide of carbon, and rapidly absorb moisture from the air. It melts at 55° C., and crystallizes in well-defined prisms on cooling. At a higher temperature, it is decomposed, giving off vapours of iodine. Water decomposes it, with formation of hydriodic and phosphorous acids, and formation of an orange-yellow flaky deposit. (Corenwinder.)‡

Estimation and separation of Chlorine, Bromine, and Iodine. — *Chlorine*, in the form of hydrochloric acid or a soluble chloride, is estimated by precipitation with nitrate of silver, the precipitate being treated in the manner described at page 600. The fused chloride contains 24·72 per cent. of chlorine, equivalent to 25·42 of hydrochloric acid.

Many chlorides, chiefly basic or oxychlorides, which are insoluble in water dissolve in nitric acid. The chlorine in such compounds may be precipitated by adding nitrate of silver to the nitric acid solution. Care must, however, be taken not to heat the compound with excess of nitric acid, as in that case a portion of the chlorine may be lost. Some chlorides, as the chloride of silver and dichloride of mercury, are insoluble even in nitric acid. Chloride of silver may be decomposed, either by ignition in a current of hydrogen, by heating it in a porcelain crucible with a mixture of the carbonates of potash and soda, in equivalent proportions, till the salt just begins to melt, or by treating it with dilute sulphuric acid in contact with a piece of pure zinc (p. 597). Dichloride of mercury is easily decomposed by caustic alkalies.

Chlorates and other oxygen-salts of chlorine may be reduced to chlorides, by ignition, or, better in most cases, by the action of sulphurous or hydrosulphuric acid. The chlorine is then precipitated by nitrate of silver, as above, after the

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* Chem. Soc. Qu. J. vi. 90.

† Ibid. vii. 51.

‡ Ann. Ch. Phys. [3], xxx. 242.

excess of the reducing agent has been removed by means of nitric acid or a ferric salt. [For the methods of determining the quantity of chlorine in bleaching powder and other hypochlorites for commercial purposes, see p. 437, and p. 801; also Bunsen's volumetric method, p. 413.]

The quantity of chlorine in an organic compound is determined by igniting the compound with excess of pure quick-lime in a combustion-tube, whereby the chlorine is converted into chloride of calcium. The contents of the tube are then dissolved in dilute nitric acid, and the chlorine precipitated by nitrate of silver.

Bromine is estimated in the form of bromide of silver (containing 42·55 per cent. of bromine), in exactly the same manner as chlorine. Bromates are also reduced to bromides in the same manner as chlorates to chlorides.

When bromine and chlorine occur together, they may both be precipitated by treating the solution with excess of nitrate of silver. The precipitate of chloride and bromide is then ignited and weighed; and a known portion of it is afterwards heated in a current of chlorine gas. The bromide of silver is thereby converted into chloride, the bromine passing off in vapour. The resulting chloride of silver weighs less than the mixture of chloride and bromide by the difference (w) between the weight of the bromine which has escaped and the chlorine which has taken its place; moreover, these weights are to one another as the equivalent weights of bromine and chlorine, that is, as 80 to 35·5. Hence, to determine the quantities of Br and Cl in the mixed silver-salts, we have the two equations,

$$\mathrm{Br} - \mathrm{Cl} = w; \quad \frac{\mathrm{Br}}{\mathrm{Cl}} = \frac{80}{355}$$

whence $$\mathrm{Br} = 1{\cdot}8\, w; \quad \mathrm{Cl} = 0{\cdot}8\, w.$$

If the quantity of bromine is very small, as in sea-water and salt-springs, in comparison with that of the chlorine, this method does not give very exact results. In such cases it is best to mix the solution, after due concentration, with only enough nitrate of silver to precipitate about one-sixth of the chlorine, and treat the precipitate thus formed,—which is sure to contain the whole of the bromine,—in the manner just described. The remainder of the chlorine is then determined by treating the filtered liquid with excess of nitrate of silver.

According to Mr. F. Field,* chloride of silver is completely decomposed by agitating it with excess of bromide of potassium in solution, the silver being converted into bromide, and the whole of the chlorine passing into the solution. This mode of decomposition might therefore be used instead of the ignition of the mixed precipitate in a current of chlorine. The chloride and bromide of silver are also completely decomposed by iodide of potassium.

Iodine in soluble iodides is estimated by precipitation with nitrate of silver, in the same manner as chlorine and bromine; 100 pts. of iodide of silver contain 54·025 pts. of iodine.

It may also be precipitated as iodide of palladium by mixing the solution with nitrate or chloride of palladium. A black precipitate then falls, which settles down slowly but completely, and when ignited, leaves metallic palladium, 100 pts. of which are equivalent to 23·83 pts. of iodine; or the precipitate may be collected on a weighed filter, dried at 100° C. and weighed; 100 pts. of it contain 7·04 pts. of iodine; but the method by ignition is to be preferred.

This method of precipitation serves also to separate iodine from bromine and chlorine. If the chlorine is also to be estimated, the precipitation must of course be made with nitrate of palladium, not with the chloride. If bromine is present without chlorine, the iodine must be precipitated with chloride of palladium, because the nitrate would precipitate bromine as well as iodine: the precipitation of the bromine may, however, be prevented by the addition of a soluble chloride. To estimate the chlorine and bromine in the filtered liquid, the excess of palladium

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* Chem. Soc. Qu. J. x. 234.

must be removed by hydrosulphuric acid, and the excess of the latter by means of nitric acid or a ferric salt. The bromine and chlorine may then be precipitated by nitrate of silver, and the precipitate treated in the manner already described.

The methods of treating insoluble iodides are similar to those already given for chlorides (p. 798).

Iodates and periodates are reduced to iodides by the action of sulphurous or hydrosulphuric acid. To decompose them by ignition would not give accurate results, because a portion of the iodine is thereby expelled.

Iodine and bromine in organic compounds are estimated in the same manner as chlorine (p. 799).

FLUORINE.

Sources of Fluorine.—Professor G. Wilson, of Edinburgh, has discovered fluorine in a great number of plants, especially in the siliceous stems of grasses and equisetaceous plants, always however in very small and variable quantities. He supposes that soluble fluorine-compounds diffuse themselves through the rising sap of the plant, and are converted, by the silica therein contained, into insoluble silico-fluorides. Traces of fluorine also occur in the trap-rocks near Edinburgh and in the neighbourhood of the Clyde, in the granites of Aberdeenshire, and in the soils formed by the disintegration of such rocks.* The same chemist has likewise found fluorine in the ashes of ox-blood, milk, cream-cheese, and very slight traces in the ash of the whey.† For the detection of small quantities of fluorine in rocks, ashes, &c., Professor Wilson heats the substance (mixed with silica if that body be not already present) with strong sulphuric acid in a glass vessel; passes the evolved fluoride of silicon into water; supersaturates the hydrofluosilicic acid thus formed with ammonia; evaporates to dryness; exhausts the residue with water; again evaporates the filtrate; and tests the residue in the ordinary way by treating it with sulphuric acid in a platinum vessel covered with a waxed glass plate.‡

Isolation of Fluorine.—Fremy, by submitting fused fluoride of potassium to the action of the voltaic battery, has eliminated a gas which rapidly attacks platinum, decomposes water with formation of hydrofluoric acid, and displaces iodine from its combinations with metals. By decomposing fluoride of calcium at a red heat with dry chlorine or oxygen, he likewise obtains a gas which rapidly attacks glass. This gas appears to be fluorine.§

Anhydrous hydrofluoric acid may be obtained by heating the fluoride of potassium and hydrogen in a platinum vessel, or by decomposing fluoride of lead on a layer of charcoal in a platinum tube by dry hydrogen gas. It is gaseous at ordinary temperatures; but at the temperature of a mixture of ice and salt, it condenses into a very mobile liquid, which acts violently on water, forms white fumes in the air, and attacks glass. (Fremy.‖)

Estimation of Fluorine.—The solid compounds of fluorine are decomposed by heating them in a platinum crucible with strong sulphuric acid, the heat being continued till all the fluorine is expelled in the form of hydrofluoric acid, and the excess of sulphuric acid is likewise drawn off. The residual sulphate is then weighed, and the quantity of metal in it calculated; this quantity deducted from the original weight of the fluorine gives the quantity of fluorine. Or, supposing no other volatile acid to be present, if the difference in the weight of the fluoride and the sulphate formed from it be d, the quantity of fluorine may be found by means of the equations,

$$SO_4 - F = d; \ \frac{SO_4}{F} = \frac{48}{18{\cdot}7}.$$

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* Edinb. Phil. J. liii. 356.

† Chem. Gaz. 1850, 366.

‡ Chem. Soc. Qu. J. v. 151.

§ Compt. rend. xxxviii. 393; xl. 966.

‖ Ibid. xxxviii. 393.

The second mode of calculation is equally applicable, whether the fluorine be combined with one metal or with several.

Fluorides frequently occur in nature in conjunction with phosphates, as in apatite and in bones. To analyze such a compound, it is first heated with sulphuric acid to expel the fluorine; the residue digested with alcohol to dissolve the phosphoric acid which has been set free; the quantity of that acid determined by precipitation with ammonia and sulphate of magnesia; and the metals now remaining in the form of sulphates determined by methods already given. Lastly, the total weight of these metals, together with that of the phosphoric acid, or rather of the corresponding salt-radical (PO_8, if the phosphates are tribasic), is deducted from the original weight of the mineral; and the difference gives the quantity of fluorine.

From solutions, fluorine is generally precipitated as fluoride of calcium, from the weight of which, if pure, the quantity of fluorine may be immediately calculated; but if other substances are precipitated at the same time, the quantity of fluorine must be determined in the manner above described.

BUNSEN'S GENERAL METHOD OF VOLUMETRIC ANALYSIS.

This method, which is applicable to a great number of analyses depending upon oxidation and reduction, is founded on the principle of liberating a quantity of iodine equivalent to the substance which is to be estimated, and determining the amount of this iodine by means of a standard solution of sulphurous acid.

Iodine and sulphurous acid, in presence of water, form hydriodic and sulphuric acids;

$$SO_2 + I + HO = SO_3 + HI,$$

each equivalent of sulphurous acid thus transformed corresponding to 1 eq. of iodine, or 32 parts by weight of anhydrous sulphurous acid to 123·36 parts of iodine.

For this reaction, however, it is necessary that the liquids be very dilute; for, at a certain degree of concentration, the opposite change takes place, sulphuric and hydriodic acids decomposing each other in such a manner as to yield sulphurous acid, water, and iodine. The solution of sulphurous acid used for the estimation of iodine must never contain more than from 0·04 to 0·05 per cent. of iodine.

The method requires three standard test-liquids: a solution of iodine, a solution of sulphurous acid, and a solution of iodide of potassium. To prepare the first, a weighed quantity of iodine, as pure as can be obtained, is dissolved in a concentrated solution of iodide of potassium (which must be perfectly free from free iodine and iodate of potash, and therefore must not exhibit any brown colour, either by itself or on addition of hydrochloric acid), and the liquid diluted to such a degree that 200 cubic centimeters may contain 1 gramme of iodine, so that, if a division of the burette contains half a cubic centimeter, each degree may contain $\frac{1}{400}$ or 0·0025 of a gramme of the iodine used. But as a commercial iodine, even the purest, contains traces of chlorine, it is necessary to determine the real value in iodine of a degree of the burette by special experiment. The method of doing this will be presently described (p. 804).

Of the second test-liquid, the dilute sulphurous acid, it is best to prepare a considerable quantity, 20 or 30 litres, at a time, so that the alteration produced in it by the oxidizing action of the air during the course of an experiment, or even in a day, may be imperceptibly small. To give the acid the proper degree of solution, 20 or 30 litres of water are mixed with a small measure-glassful of concentrated sulphurous acid; the liquid shaken; 200 burette-degrees, or 100 cubic centim. of it measured off; this portion of liquid mixed with starch, and the standard solution of iodine added from the burette, till the liquid just exhibits a perceptible blue colour. If the number of burette-degrees of the iodine-solution required for this purpose be t, and the quantity of iodine in one degree be a, the quantity, x, of anhydrous sulphurous acid, $\ddot{\text{S}}$, in 100 degrees of the acid solution will be

$$x = \frac{\ddot{\text{S}}}{\text{I}} . at = \frac{32}{126{\cdot}36} . at.$$

The most convenient strength of the sulphurous acid solution is about 0·03 anhydrous sulphurous acid to 100 water.* It must be tested at the commencement of each day's work, and will require renewal after three or four days.†

The third test-liquid is a solution of pure iodide of potassium, containing about 1 grm. of the iodide to 10 cubic centimeters of water.

1. *Determination of the amount of pure iodine in a commercial sample.*—The weighed sample is dissolved in the solution of iodide of potassium, in the proportion of about 0·1 grm. to 4 or 5 cub. centim. of liquid. To the resulting brown solution, as many measures, n, of the standard-solution of sulphurous acid are added as are required to destroy the brown colour completely. The next step is to determine the quantity of iodine, x, by which this quantity of sulphurous acid has been partially decomposed. This is effected by adding three or four cubic centimeters of clear and very dilute starch-solution, and then dropping in the standard-solution of iodine from the burette, till a blue colour begins to appear. If t' degrees of the iodine-solution are required for this purpose, and the quantity of iodine in each degree is a, the quantity required to decompose completely the n measures of sulphurous acid is $x + at'$. Further, if we determine the quantity of iodine, $a\,t$, required to decompose one measure of the sulphurous acid solution, we shall obtain the equation $x + at' = nat$; whence

$$x = a\,(nt - t').$$

If the weight of the sample of iodine be A, the quantity expressed as a per centage will be $\frac{100a}{A}\,(nt - t')$; and if $\frac{100a}{A} = 1$, that is, if the quantity weighed out is exactly 100 a (4 grms. if $a = \frac{1}{400}$ grm.), the difference of the two measurements, $nt - t'$, gives at once the per centage of iodine in the sample.

The same method may be applied to determine the quantity of free iodine contained in any liquid.

2. *Determination of Chlorine.* — Chlorine decomposes a solution of iodide of potassium instantly and completely, without the aid of heat, setting free an equivalent quantity of iodine. If this quantity of liberated iodine be determined in the manner just described, the quantity of chlorine will be given by the equation,

$$x = \frac{\text{Cl}}{\text{I}}\,a\,(nt - t').$$

3. Similarly for *Bromine:*

$$x = \frac{\text{Br}}{\text{I}} . a\,(nt - t').$$

4. *Chlorine and Bromine together.*—To estimate the quantity of chlorine contained in a sample of bromine, a quantity, A, of the bromine, throughly dried, is dissolved in a solution of iodide of potassium, and the quantity of iodine, $a(nt - t')$ thereby separated, is determined as above. Then, denoting the quantity of bromine by x, and that of chlorine by y, we have the equations: —

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* As a cubic centimeter of water weighs a gramme, this is the same as 0·03 grm. in 100 cubic centimeters or 200 burette-divisions.

† A modification of this method, in which hyposulphite of soda is used instead of sulphurous acid, has been introduced by Mr. E. O. Brown. (See page 484.)

$$x + y = A;$$

$$\frac{\mathrm{I}}{\mathrm{Br}}x + \frac{\mathrm{I}}{\mathrm{Cl}}y = a\,(nt - t');$$

$$\text{whence } x = \frac{\frac{\mathrm{I}}{\mathrm{Cl}}A - a\,(nt - t')}{\frac{\mathrm{I}}{\mathrm{Cl}} - \frac{\mathrm{I}}{\mathrm{Br}}};\ y = \frac{a\,(nt - t') - \frac{\mathrm{I}}{\mathrm{Br}}A}{\frac{\mathrm{I}}{\mathrm{Cl}} - \frac{\mathrm{I}}{\mathrm{Br}}}.$$

If the chlorine and bromine are in a state of combination, they may be set free by distilling the mixture or compound with bichromate of potash and sulphuric acid, the evolved gases being passed into the solution of iodide of potassium.

A similar method may be applied to a mixture of chlorine and iodine, the equations then becoming —

$$x + y = A;\ \frac{\mathrm{I}}{\mathrm{Cl}}x + y = a\,(nt - t').$$

5. *Chlorites and Hypochlorites.*—A solution of the salt is mixed with solution of iodide of potassium, and hydrochloric acid added in slight excess. From the quantity of iodine, $a\,(nt - t')$ thus separated, the quantity of chlorous acid, x', or hydrochlorous acid, x'', may be determined from the equations

$$x' = \frac{\dddot{\mathrm{Cl}}}{4\mathrm{I}}\,a\,(nt - t');$$

$$x'' = \frac{\dot{\mathrm{Cl}}}{2\mathrm{I}}\,a\,(nt - t').$$

It must be remembered that 1 eq. ClO decomposes 2 eq. Kl, and 1 eq. $\mathrm{ClO_3}$ decomposes 4KI.

This method is well adapted to the estimation of chloride of lime for commercial purposes. If A be the weight of the sample, the percentage of chlorine will be $\frac{100\ \mathrm{Cl}}{A\,.\,\mathrm{I}}\,a\,(nt - t')$; and if A be equal to $\frac{100\ \mathrm{Cl}}{\mathrm{I}}\,a$, the difference of the two measurements, $nt - t'$, gives directly the bleaching power of the product in percentage of chlorine.

6. *Chromates.* — When a chromate, *e.g.* bichromate of potash, is boiled with excess of fuming hydrochloric acid, every 2 eq. chromic acid eliminate 3 eq. chlorine: —

$$2\mathrm{CrO_3} + 6\mathrm{HCl} = \mathrm{Cr_2Cl_3} + 6\mathrm{HO} + 3\mathrm{Cl};$$

and the 3 eq. of chlorine passed into a solution of iodide of potassium, liberate 3 eq. of iodine, which may be estimated volumetrically as above. Hence the quantity x of chromic acid contained in a known weight A of bichromate of potash, or any other chromate, will be given by the equation —

$$x = \frac{2\ \dddot{\mathrm{Cr}}}{3\mathrm{I}}\,a\,(nt - t');$$

$$\text{or in 100 parts: } x = \frac{200\ \dddot{\mathrm{Cr}}}{A\,.\,3\mathrm{I}}\,a\,(nt - t').$$

If $A = \frac{200\ \dddot{\mathrm{Cr}}}{3\mathrm{I}}\,a$, that is, if the sample taken weighs exactly this quantity, the difference of the two measurements, $nt - t'$, gives directly the percentage of chromic acid. Similarly, for $A = 100\,\frac{\dot{\mathrm{K}} + 2\dddot{\mathrm{Cr}}}{3\mathrm{I}}\,a$, this difference would give the percentage of pure bichromate of potash, and for $A = 200 \frac{Pb + \dddot{Cr}}{3I} a$, the percentage of pure chromate of lead in these respective salts.

The analysis is made by introducing a weighed quantity of the chromate into a small flask holding about 40 cubic centimeters, filled about two-thirds with fuming hydrochloric acid, and having a gas-delivery tube adapted to its neck by means of a tube of vulcanized caoutchouc. The glass tube is inserted into the neck of an inverted retort, of the capacity of about 160 cubic centim., containing a solution of iodide of potassium. The middle of the neck of the retort is blown out into a bulb to receive any liquid that may be thrown up. A piece of vulcanized caoutchouc is tied tightly over the open end of the glass tube, and a slit cut in it with a sharp, wet penknife. This slit opens when pressed from within, but closes tightly when pressed in the opposite direction, thus forming an excellent valve. The liquid in the flask is now boiled for three or four minutes, by which time the whole of the chlorine is expelled, and an equivalent quantity of iodine liberated.

The volumetric analysis of pure bichromate of potash affords an easy method of determining the value of a, or the quantity of pure iodine contained in a burette degree of the standard solution (p. 802). For if the bichromate of potash be pure, its weight A is exactly equal to $\frac{\dot{K} + 2\dddot{Cr}}{3I} a\,(nt - t')$; therefore,

$$a = \frac{3IA}{(\dot{K} + 2\,\dddot{Cr})\,(nt - t')}.$$

7. *Peroxides.* — The quantity of oxygen in the peroxides of lead, manganese, &c., may be estimated in a similar manner to chromic acid. Thus, the percentage of oxygen in binoxide of lead PbO_2 is given by the formula —

$$x = 100\,\frac{2O}{A\,.\,I}\,a\,(nt - t');$$

and the percentage of pure binoxide of manganese in a commercial sample of the black oxide by the formula —

$$x = \frac{100\,\ddot{Mn}}{A\,.\,I}\,a\,(nt - t').$$

Besides the preceding and a great number of other bodies which give rise to a separation of free chlorine, the iodometric method may be applied to the estimation of substances which are raised by chlorine to a higher degree of oxidation. These substances are heated with fuming hydrochloric acid and a known weight, p, of pure bichromate of potash; the evolved chlorine is passed into iodide of potassium; and the liberated iodine estimated as above. The quantity thus separated, viz. $a\,(nt - t')$, is equal to the quantity of iodine, $\frac{p\,.\,3I}{\dot{K} + 2\dddot{Cr}}$, equivalent to the bichromate used *minus* the quantity i, equivalent to the protoxide to be estimated. The latter is therefore,

$$i = \frac{p\,.\,3I}{\dot{K} + 2\dddot{Cr}} - a\,(nt - t').$$

Thus, to determine the amount of protoxide of iron in a given sample of iron-ore, it must be remembered that each equivalent of iodine or chlorine converts 2 eq. of protoxide into sesquioxide: —

$$2FeO + I + HO = Fe_2O_3 + HI.$$

If then i be the quantity of iodine required to convert the protoxide of iron in a given sample into sesquioxide, the quantity e of protoxide in this sample will be $e = i \, . \, \frac{2\dot{\mathrm{Fe}}}{\mathrm{I}}$; and substituting for i its value above given, we have

$$e = \frac{6\ \dot{\mathrm{Fe}}}{\dot{\mathrm{K}} + 2\dddot{\mathrm{Cr}}}\, p - \frac{2\ \dot{\mathrm{Fe}}}{\mathrm{I}}\, a\, (nt - t');$$

and hence it is easy to calculate the equivalent quantities of metallic iron and sesquioxide.

Various other applications of the method, will be found in Professor Bunsen's memoir.*

METALS OF THE ALKALIES AND EARTHS.

POTASSIUM.

Preparation of Potassium.—The process of obtaining this metal by igniting a mixture of carbonate of potash and charcoal, has received considerable improvements from the researches of Maresca and Donny.† The ordinary form of the process, which is that devised by Brunner, is dangerous, and gives very uncertain results, the quantity of metal obtained by it being often very small, and sometimes, even when the greatest care is taken, absolutely nothing. The danger arises from the obstruction of the connecting tube by the black substance formed by the action of carbonic oxide on the potassium there deposited; and the loss of product is due, partly to the formation of this black substance, and partly to the escape of portions of the metal in the form of vapour. The first of these inconveniences can only be obviated by keeping the entire length of the connecting tube at a red heat during the whole operation. But in that case, if the large receivers invented by Brunner (see fig. 152, p. 370, and 153, p. 371,) are used, not a particle of the metal condenses, the whole escaping in the form of vapour. Hence it is necessary to use much smaller receivers; and the form which the authors find to give the best results, is that of a shallow rectangular box, 12 centimeters long, 6 wide and 4 deep. Another source of failure in the operation is the want of a due proportion between the carbonate of potash and charcoal in the calcined tartar. To obtain the best result, the quantity of charcoal should be neither more nor less than that which is theoretically required for the complete reduction of the potash present. Whether this is the case, can only be ascertained by a previous analysis of the burnt tartar; and any excess or deficiency of charcoal, must be remedied by mixing samples of tartar of different qualities. Lastly, to prevent the perforation of the iron bottle during the ignition, it should be coated, not with clay luting, but with fused borax. Such a coating is easily formed by sprinkling pulverized borax on the bottle when it is at a dull red heat.

Preparation of Potassium by Electrolysis. — A mixture of 1 at. chloride of potassium and 1 at. chloride of calcium (which mixture is used because it melts at a much lower temperature than chloride of potassium alone), is melted in a small porcelain crucible over a lamp, and subjected to the action of a Bunsen's battery of six elements with carbon poles, the heat being so regulated that a solid crust forms round the negative carbon pole, while the mixture remains fused and allows the free evolution of chlorine at the positive pole. When the decomposition has been continued in this manner for about twenty minutes, and the cooled

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* Ann. Ch. Pharm. lxxxvi. 265; Chem. Soc. Qu. J. viii. 218.

† Ann. Ch. Phys. [3], xxxv. 147.

crucible is opened under rock-oil, a large quantity of potassium, almost chemically pure, is generally obtained. If the same experiment be repeated at a white heat over a charcoal fire, with an iron wire as negative pole, small globules of potassium are seen burning on the surface; and these, when analyzed, are found to be almost pure. (Matthiessen.)*

Preparation of pure Hydrate of Potash.—Wöhler recommends for this purpose the decomposition of pure nitre by metallic copper at a red heat. 1 pt. of nitre and 2 or 3 pts. of thin copper plate cut into small pieces, are arranged in alternate thin layers in a covered copper crucible, and exposed for half an hour to a moderate red heat. The cooled mass is then treated with water, the liquid left to stand in a tall covered cylindrical vessel till the oxide of copper has completely settled down, and the pure solution of potash then decanted with a siphon.

With the above proportions of nitre and copper part of the latter is converted only into suboxide. It may, therefore, be used for a second preparation of potash, by mixing 1 pt. of it with 1 pt. of nitre and 1 pt. of metallic copper.

Iron may also be used to decompose the nitre; but the potash thereby obtained is contaminated with small quantities of carbonic acid, silica, &c. The same objection applies to the use of an iron crucible, if a perfectly pure product be required.†

Estimation of Potassium. Potassium, when it occurs in a compound not containing any other metal, may be estimated either as sulphate or as chloride. All potassium-salts containing volatile acids, are decomposed by heating them with sulphuric acid, the excess of which may afterwards be expelled by a stronger heat, and the quantity of potassium or potash calculated from the weight of the residual neutral sulphate. It is difficult, however, to expel the last traces of free sulphuric acid by mere ignition; but they may be completely driven off by dropping a lump of carbonate of ammonia into the crucible, and repeating the ignition with the cover on; the sulphuric acid then diffuses into the atmosphere of ammonia in the crucible, and a perfectly neutral sulphate remains. It contains 54·06 per cent. of potash, KO.

In estimating potassium as chloride, the only precaution to be observed is to ignite the chloride in a covered crucible, as, when strongly heated in contact with the air, a portion of it volatilizes. The chloride contains 52·47 per cent. of potassium, equivalent to 63·19 per cent. of potash.

The separation of potassium from all soluble substances except ammonia, is easily effected by precipitating it with bichloride of platinum, adding alcohol to complete the precipitation of the chloroplatinate of potassium, collecting the precipitate on a weighed filter, washing with alcohol, and drying it at 100° C. It contains 16·04 per cent. of potassium, equivalent to 19·31 of potash.

SODIUM.

Preparation.—Deville finds that the reduction of this metal from the carbonate, by ignition with charcoal, is greatly facilitated by the addition of some substance, such as chalk, which retains the mass in a pasty state during ignition. The best product is obtained with a mixture of 717 pts. of dry carbonate of soda, 175 charcoal, and 108 chalk. With regard to the form of apparatus, and the mode of conducting the process, Deville follows exactly the directions given by Maresca and Donny (p. 805), for the preparation of potassium.‡

Sodium may be readily obtained by electrolysis, in a manner similar to that described for potassium (p. 805), using, however, a mixture of 1 at. chloride of sodium, and 2 at. chloride of calcium. (Matthiessen.)

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* Chem. Soc. Qu. J. viii. 30.

† Ann. Ch. Pharm. lxxxvii. 373.

‡ Ann. Ch. Phys. [3], xliii. 5.

Carbonate of Soda. — Solutions of carbonate of soda are capable of assuming the state of supersaturation, and exhibiting phenomena similar to those of the sulphate (p. 391). An aqueous solution of the salt, saturated at a high temperature, and enclosed while boiling hot in sealed tubes or well-corked flasks, remains supersaturated at ordinary temperatures, and frequently, even when cooled several degrees below 0° C., not depositing any crystals. Keeping the air in contact with the liquid from agitation (as by covering the hot solution with a glass receiver), is often sufficient to prevent the formation of crystals at ordinary temperatures; but free access of air causes immediate solidification, attended with rise of temperature. The passage of an electric current through a supersaturated solution, does not induce any change of state.

The supersaturated solutions of carbonate of soda contain a salt having less water of crystallization than the ordinary 10-hydrated salt. The salt contained in them is, in fact, a 7-hydrated salt, $NaO . CO_2 + 7HO$, and of this salt there are two modifications, differing in crystalline form and in degree of solubility. One of them (*a*) crystallizes in rhombohedral crystals; the other (*b*), in square tables or low prisms: both these salts absorb water rapidly. The salt *b* was first obtained by Thomson, who, however, supposed it to contain 8 at. water. When a solution saturated at the boiling heat, and containing a slight excess of the solid salt, is enclosed in a flask, which is corked immediately after the boiling has ceased, no crystals are deposited from it for a long time on cooling down to between 25° and 18° C.; but on cooling below 8°, it deposits chiefly the salt *b*. When cooled to between 16° and 10°, it yields the salt *a*, which redissolves between 21° and 22°, forms again on cooling to 19°; and on cooling from 10° to 4°, becomes opaque, and passes into the salt *b*. After cooling to a lower temperature, and for a longer time, when the state of supersaturation ceases, the whole is converted into a mass of crystals of the ordinary salt $NaO . CO_2 + 10$ aq. The following table gives a comparative view of the quantities of the 10-hydrated and of the two varieties of the 7-hydrated salt, contained in 100 parts of the saturated solutions at different temperatures: —

Temperature............	0°	10°	15°	20°	25°	30°	38°	104°.
10-hydrated salt........	7·0	12·1	16·2	21·7	28·5	37·2	51·7	45·5.
7-hydrated (*b*).....	20·4	26·3	29·6	38·6	38·1	43·5	—	—
7-hydrated (*a*)..........	31·9	37·9	41·6	45·8	—	—	—	—

Hence, it appears, that carbonate of soda exhibits a maximum of solubility, at 38° C. The decrease of solubility above this point arises from the formation of another hydrate, $NaO . CO_2 + HO$. This hydrate, which separates out when a solution saturated at 104° C. is concentrated by boiling, is more soluble in cold than in hot water, and the crystals which have been separated by boiling, redissolve in the mother liquor, when left to cool in a closed vessel. (H. Loewel.)*

Besides the hydrates above-mentioned, two others have been discovered by Jacquelain,† viz. $NaO . CO_2 + 15HO$, which crystallizes below — 20°, and when dried in vacuo gives off 5 atoms of water, and is converted into the ordinary ten-hydrated salt; and $NaO . CO + 9HO$, obtained by repeatedly crystallizing a solution which at first contains a portion of bicarbonate of soda. Jacquelain also finds that carbonate of soda gives off carbonic acid when melted, even in a stream of pure and dry carbonic acid.

Sulphate of Soda. — This salt appears to be capable of existing in solution in three different states, viz. as anhydrous salt, $NaO . SO_3$, as the seven-hydrated salt, $NaO . SO_3 + 7HO$, and as the ten-hydrated salt, $NaO . SO_3 + 10HO$, which is the ordinary Glauber's salt. The following table shows the solubility (as determined by Loewel‡) of the anhydrous salt, and of the two hydrates, in water, at various temperatures; also the quantity of anhydrous salt corresponding in each

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* Ann. Ch. Phys. [3], xxxiii. 334.

† Compt. rend. xxx. 106.

‡ Ann. Ch. Phys. [3], xlix. 32.

case to the hydrate dissolved. The numbers in the table are the quantities of salt dissolved in 100 parts of water.

SOLUBILITY OF SULPHATE OF SODA.

Temp.	$NaO.SO_3$.	$NaOSO_3 + 10HO$.		$NaO.SO_3 + 7HO$.	
	Anhydrous.	Anhydrous.	Hydrate.	Anhydrous.	Hydrate.
0° C.	....	5·02	12·16	19·62	44·84
10	....	9·00	23·04	30·49	78·90
15	....	13·20	35·96	37·43	105·79
18	52·25	16·80	48·41	41·63	124·59
20	52·76	19·40	58·35	44·73	140·01
25	51·53	28·00	98·48	52·94	188·46
26	51·31	30·00	109·81	54·07	202·61
30	50·37	40·00	184·09		
33	49·71	50·76	323·13		
34	49·53	55·00	412·22		
40·15	48·78				
50·40	46·82				
59·79	45·42				
70·61	44·35				
84·42	42·96				
103·17	42·65				

Sulphate of Soda and Potash.—Gladstone* has obtained a salt containing $\left.\begin{matrix}5KO\\NaO\end{matrix}\right\}6SO_3$, by fusing the neutral or acid sulphate of potash with chloride of sodium, or sulphate of potash with sulphate of soda, dissolving the fused mass in hot water, and leaving it to crystallize, or by mixing the two salts in hot aqueous solution. The salt which crystallized out was anhydrous, and exhibited the crystalline form of sulphate of potash. H. Rose† had previously obtained the same salt, but had not assured himself of its definite constitution.

Estimation of Sodium.—This metal, like potassium, may be estimated either as chloride or as sulphate. The sulphate contains 32·54, and the chloride 39·53 per cent. of sodium.

Sodium is separated from potassium by means of bichloride of platinum, with addition of alcohol, which precipitates the potassium, and leaves the sodium in solution. The quantity of potassium may then be determined from the weight of the precipitate, and the sodium estimated by difference. Or if a direct estimation of the sodium be desired, the filtered liquid may be freed from excess of platinum by means of hydrosulphuric acid, and the sodium in the filtrate, which then contains no other metal, determined as sulphate.

If the potassium and sodium are in the form of chlorides, the method just described may be applied immediately; if not, it is best first to convert them into chlorides, which may in some cases be done by merely heating the mixed salts with excess of hydrochloric acid, or, in case of sulphuric or phosphoric acid being present, by precipitating the acid with chloride of barium, removing the excess of barium with carbonate of ammonia, and expelling the ammoniacal salts from the filtrate by evaporation and ignition. The residue is a mixture of the chlorides of potassium and sodium.

AMMONIUM.

A compound radical consisting of ammonia with an additional atom of hydrogen, was first supposed to exist in the ordinary salts of ammonia by Berzelius, and

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* Chem. Soc. Qu. J. vi. 106.

† Pogg. Ann. lii. 452.

termed ammonium. This body has never been insulated, but is supposed to appear, in a certain experiment, in combination with mercury, and possessed of the metallic character (p. 167). The compounds of ammonium are always strictly isomorphous with the corresponding compounds of potassium.

Chloride of ammonium, Hydrochlorate or Muriate of ammonia, Sal-ammoniac, $NH_4 . Cl$. — This salt is formed when ammonia is neutralized by hydrochloric acid; $NH_3 + HCl = NH_4 . Cl$. It is prepared in large quantity from the ammoniacal liquor obtained in the distillation of bones, in the manufacture of animal charcoal, and from the liquor which condenses in the distillation of coal for gas. These liquors contain ammonia principally in the state of carbonate and hydrosulphate, which may be converted into chloride of ammonium by the addition of hydrochloric acid. The salt is purified by crystallization, and sublimed in vessels of iron or earthenware, in the upper part of which it condenses and forms a solid cake, the condition in which sal ammoniac is always met with in commerce.

Sal-ammoniac is tenacious and difficult to reduce to powder; its sp. gr. is 1·45. It has a sharp and acrid taste, and dissolves in 2·72 parts of cold, and in an equal weight of boiling water; it is also soluble in alcohol. It generally crystallizes from solution in feathery crystals, which are formed of rows of minute octohedrons attached by their extremities. At a red heat it volatilizes without previous fusion.

A corresponding bromide, iodide, and fluoride of ammonium may be formed by neutralizing ammonia with hydrobromic, hydriodic, and hydrofluoric acids.

Sulphides of Ammonium.—When 4 volumes of ammonia combine with 2 of hydrosulphuric acid gas, the sulphide of ammonium is produced; $NH_3 + HS = NH_4 . S$. Ammonium combines with sulphur in several other proportions, which are obtained on mixing and distilling the various sulphides of potassium with sal-ammoniac. In the reciprocal decomposition which occurs, the potassium combines simply with chlorine, and the ammonium with sulphur. The following compounds are generally enumerated: $NH_4 . S$; $NH_4 . S + HS$; $NH_4 . S_3$ and $NH_4 . S_5$. The protosulphide has long been formed by distilling a mixture of quicklime, sulphur, and sal-ammoniac, and known under the name of the *fuming liquor of Boyle.* It is a volatile liquid, the vapour of which is decomposed by oxygen, and thus fumes produced. The second compound, which is a sulphide of hydrogen and ammonium, is formed by transmitting hydrosulphuric acid gas through solution of ammonia to saturation. This liquid is generally called the hydrosulphate of ammonia, and is a very useful reagent in chemical analysis. All the sulphides of ammonium are soluble in water and alcohol without decomposition.

Nitrate of Ammonium, $NH_4O . NO_5$.—When nitric acid is saturated with ammonia, a salt is obtained which crystallizes in six-sided prisms, and is isomorphous with nitrate of potash. Besides the elements of anhydrous nitric acid and ammonia, this salt contains an atom of water which cannot be separated from it, which is also found in, and is equally essential to, the salts formed by neutralizing all other oxygen-acids by ammonia, such as sulphurous acid, sulphuric, carbonic, &c., in contact with water. The hydrogen of this water is assigned to the ammonia, to form ammonium, which the oxygen converts into oxide of ammonium, so that the product is nitrate of the oxide of ammonium; or $NH_3 + HO . NO_5 = NH_4O . NO_5$. This salt deflagrates with flame when thrown upon red-hot coals When decomposed between 300° and 400°, it is resolved into water and nitrous oxide (p. 597).

Carbonates of Ammonium. — The neutral carbonate of oxide of ammonium appears not to exist in the free state, but by distilling the sesquicarbonate of ammonia of the shops at a gentle heat, Rose obtained a volatile crystalline salt, which may be viewed as a compound of anhydrous carbonate of ammonia with carbonate of ammonium: $NH_3 . CO_2 + NH_4O . CO_2$. When the commercial salt is exposed to the air, it loses its pungent odour, and a white friable mass remains, which is the bicarbonate of ammonium, or carbonate of water and oxide of ammonium: $HO . CO_2 + NH_4O . CO_2$. This is a stable salt, and may be dissolved and crystallized without change.

The sesquicarbonate of ammonia of the shops is a crystalline transparent mass, which Rose finds to have generally, but not always, the composition assigned to it by Mr. Phillips, or to contain $3CO_2$ with $2NH_3$ and $2HO$. Rose is disposed to consider it a compound of anhydrous carbonate of ammonia and bicarbonate of oxide of ammonium, or $NH_3CO_2 + (HO . CO_2 + NH_4 O . CO_2)$. Mr. Scanlan has shown that a small quantity of water dissolves out the carbonate from this salt, and leaves the bicarbonate, which is the least soluble. This observation does not prove the commercial salt to be a mechanical mixture of the two salts derived from it, as many undoubted compounds of two salts are decomposed by water, when one of the constituent salts is much more soluble than the other. Another salt was obtained by Rose, in well-formed crystals, of which the ammonia and carbonic acid are in the proportions of the sesquicarbonate, but with three additional atoms of water. No fewer than twelve different carbonates of ammonia are described by that chemist.*

Sulphate of Ammonium, $NH_4O . SO_3 + HO$. — This is a highly soluble salt, which possesses an atom of water of crystallization, in addition to the atom which is essential to its constitution. It appears also to crystallize without this water.

Phosphates of Ammonium. — The biammoniacal tribasic phosphate, $(2NH_4O . HO) . PO_5$, analogous to ordinary phosphate of soda, is obtained by decomposing the acid phosphate of lime with carbonate of ammonium. It forms large transparent crystals, belonging to the oblique prismatic system, which effloresce on the surface when exposed to the air, and give off a portion of their ammonia, even at ordinary temperatures. The salt dissolves in 4 parts of cold, and a smaller quantity of hot water. (Mitscherlich.)

The monoammoniacal phosphate, $(NH_4O . 2HO) . PO_5$, is formed by adding phosphoric acid to the solution of the preceding salt, till the liquid becomes slightly acid. It forms crystals belonging to the square prismatic system, and somewhat less soluble than the preceding. (Mitscherlich.)

A basic phosphate is also formed by mixing a concentrated solution of the biammoniacal salt with ammonia; but it quickly gives off ammonia, and is reconverted into the biammoniacal salt.

Pyrophosphate and *Metaphosphate of Ammonium* may also be formed by adding ammonia to the aqueous solutions of the respective acids; but they are converted by evaporation into the corresponding tribasic phosphates. (Graham.)

Oxalates of Ammonium. — The neutral oxalate, $C_4(NH_4)_2O_8$ (regarding oxalic acid as a bibasic acid, p. 702), is obtained by neutralizing the aqueous acid with ammonia It crystallizes in long prisms united in tufts and belonging to the right-prismatic system: they contain 2 eq. of water, which they give off at a moderate heat. The acid oxalate, $C_4(H . NH_4)O_8$, is precipitated in the crystalline form, when the solution of the neutral salt is mixed with oxalic, sulphuric, or hydrochloric acid. It is much less soluble than the neutral salt.

A superoxalate, $C_4(H . NH_4)O_8 + C_4H_2O_8$, separates from a solution of equal parts of oxalic acid and the acid oxalate, in crystals resembling those of the preceding salt, and containing 4 eq. of water.

Neutral oxalate of ammonium, when strongly heated, gives off 4 at water, and yields a sublimate of oxamide (p. 713):

$$\underbrace{C_4N_2H_8O_8}_{\text{Neutral oxalate of ammonium.}} - 4HO = \underbrace{C_4N_2H_4O_4}_{\text{Oxamide.}}.$$

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* Scientific Memoirs, ii. 98.

The acid salt, when heated, gives off 2 at. water, and leaves oxamic acid (p. 704):

$$\underbrace{C_4NH_5O_8}_{\text{Acid oxalate of ammonium.}} - 2HO = \underbrace{C_4NH_3O_6}_{\text{Oxamic acid.}}$$

All amides and amidogen-acids may, indeed, be regarded as ammonium-salts *minus* water. But few of them, however, are produced by the actual abstraction of water from the corresponding ammonium-salts; they are more generally produced by the action of ammonia on anhydrous acids, acid chlorides, or compound ethers (pp. 704, 713, 715).

The compounds formed by the action of dry ammonia on the anhydrous acids, sometimes called anhydrous salts of ammonia, and, by H. Rose, *ammon-salts*, are all either amides or amidogen-acids. Thus, 2 vols. ammoniacal gas, and 1 vol. carbonic acid, unite and form the compound NH_3CO_2, which, doubling the atomic weight, is *carbamide*, $N_2\left\{\begin{matrix}C_2O_2\\H_4\end{matrix}\right.$, or 2 at. ammonia in which one-third of the hydrogen is replaced by the biatomic radical carbonyl, C_2O_2. With anhydrous sulphuric acid, ammonia forms two compounds, viz. NH_3SO_3, Rose's *sulph-atammon*, or *sulphamide*, $= N_2\left\{\begin{matrix}S_2O_4\\H_4\end{matrix}\right. + 2HO$; and *sulphamic acid*, $NH_3S_2O_6 = \left.\begin{matrix}N.\overbrace{H_2(S_2O_4)}\\H\end{matrix}\right\}O_2$. Similarly, with anhydrous sulphurous acid, ammonia forms thionamide, $NH_3SO_2 = N_2\left\{\begin{matrix}S_2O_2\\H_4\end{matrix}\right.$, and thionamic acid, $NH_3S_2O_6 = \left.\begin{matrix}N.\overbrace{H_2(S_2O_2)}\\H\end{matrix}\right\}O_2$.
[*For the amides of phosphoric acid, see page* 787.]

All salts of ammonium, heated with fixed caustic alkalies, give off ammonia, which may be absorbed by hydrochloric acid, and its quantity then determined either by evaporating the solution of chloride of ammonium over the water-bath, or, more exactly, by precipitation with bichloride of platinum (p. 619).

LITHIUM.

Preparation. — Pure chloride of lithium is fused over a spirit-lamp, in a small porcelain crucible, and decomposed by a zinc-carbon battery of four or six cells. The positive pole is a small splinter of gas-coke (the hard carbon deposited in the gas-retorts), and the negative pole an iron wire about the thickness of a knitting-needle.* After a few seconds, a small silver-white regulus is formed under the fused chloride, round the iron wire and adhering to it, and after two or three minutes attains the size of a small pea. To obtain the metal, the wire pole and regulus are lifted out of the fused mass, by a small, flat, spoon-shaped iron spatula. The wire may then be withdrawn from the still melted metal, which is protected from oxidation by a coating of chloride of lithium. The metal may now be easily removed from the spatula with a penknife, after having been cooled under rock-oil. These operations may be repeated every three minutes; and thus an ounce of the chloride may be reduced in a very short time.

Lithium, on a freshly-cut surface, has the colour of silver, but quickly tarnishes on exposure to the air, becoming slightly yellow. It melts at 180° C.

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* The decomposing power of an electric current depends chiefly upon its *density, i. e.* upon the quotient obtained by dividing the strength of the current by the surface of the pole at which the electrolysis takes place. Thus, a current of constant strength passed through an aqueous solution of terchloride of chromium, eliminates, as its density is successively diminished (or the cross-section of the reducing pole increased), metallic chromium, chromous oxide, chromic oxide, and, lastly, hydrogen. (Bunsen, *Pogg. Ann.* xci. 619.)

(356° F.), and if pressed at that temperature between two glass plates, exhibits the colour and brightness of polished silver. It is harder than potassium or sodium, but softer than lead, and may, like that metal, be drawn out into wire. It tears much more easily than a lead wire of the same dimensions. It may be welded by pressure at ordinary temperatures. It swims on rock-oil, and is the lightest of all known solids, its specific gravity being only 0·5986. Taking the atomic weight at 6·5, its atomic volume is therefore 1·06, being nearly the same as that of calcium.

Lithium is much less oxidable than potassium or sodium. It makes a lead-grey streak on paper. It ignites at a temperature much higher than its melting point, burning quietly, and with an intense white light. It burns when heated in oxygen, chlorine, bromine, iodine, or dry carbonic acid, and with great brilliancy on boiling sulphur. When thrown on water, it oxidizes, but does not fuse like sodium. Nitric acid acts on it so violently, that it melts and often takes fire. Strong sulphuric acid attacks it slowly; dilute sulphuric acid and hydrochloric acid, quickly. Silica, glass, and porcelain are attacked by lithium at temperatures even below 200° C. (Bunsen.)*

According to Dr. Mallett,† the atomic weight of lithium is 6·95; and accordingly that of sodium is exactly the mean between those of lithium and potassium.

Nitrate of Lithia.—This salt has a strong tendency to form supersaturated solutions. Above 10° or 15° C., it crystallizes in rhombic prisms, resembling those of common nitre, but below 10° in rhombohedrons; both kinds of crystals are deliquescent. The crystals which separate from the supersaturated solution at 1° C. are slender needles. (Kremers.)‡

Phosphate of Lithia.—According to W. Mayer,§ the precipitate formed on adding phosphate of soda to the solution of a lithia-salt, is not a double phosphate of lithia and soda, as commonly supposed, but a tribasic phosphate of lithia, $3LiO.PO_5$ The same precipitate is also produced when a lithia-salt is treated with phosphate of potash or phosphate of ammonia, mixed with free alkali.

Estimation of Lithium.—This element, when separated from other metals, may be estimated in the form of sulphate or chloride, in the same manner as potassium or sodium. From potassium it is separated by precipitating the latter with bichloride of platinum; and from sodium, by converting the two bases into chlorides, and treating the dried chlorides, in a well-closed bottle, with a mixture of absolute alcohol and ether, which, after a few days, dissolves the whole of the chloride of lithium, and leaves the chloride of sodium undissolved.

BARIUM.

Bunsen has obtained this metal by subjecting chloride of barium, mixed up to a paste with water and a little hydrochloric acid, at a temperature of 100° C., to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner, the metal is obtained as a solid, silver-white, highly-crystalline amalgam, which, when placed in a little boat made of thoroughly ignited charcoal, and heated in a stream of hydrogen, yields barium in the form of a tumefied mass, darkly tarnished on the surface, but often exhibiting a silver-white lustre in the cavities.‖ Matthiessen has obtained barium by a method similar to that adopted for strontium (p. 690), but only in the form of a metallic powder.

Binoxide or Peroxide of Barium.—A solution of this oxide in dilute hydrochloric acid acts as a reducing agent on various metallic oxides, a portion of its oxygen uniting, at the moment of separation, with the oxygen of the other metallic

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* Ann. Ch. Pharm. xciv. 107; Chem. Soc. Qu. J. viii. 143.

† Sill. Ann. J. [2], xxii. 349.

‡ Pogg. Ann. xcii. 520.

§ Ann. Ch. Pharm. xcviii. 193.

‖ Pogg. Ann. xci. 619.

oxide (p. 689). When peroxide of barium is introduced into a solution of bichromate of potash acidulated with hydrochloric acid, oxygen is abundantly evolved (its evolution being, however, preceded, in the case of cold dilute solutions, by the formation of a blue compound, first observed by Barreswil, and supposed by him to be a perchromic acid, Cr_2O_7); and according to Brodie's experiments, the reaction, when a great excess of bichromate of potash is present, takes place as shown by the equation —

$$2CrO_3 + 4BaO_2 = Cr_2O_3 + 7O + 4BaO,$$

the chromic acid being reduced to sesquioxide of chromium. The quantity of oxygen evolved affords the means of calculating the per centage of real BaO_2 in the sample used. Oxide, chloride, sulphate, or carbonate of silver introduced into an acid solution of a peroxide of barium, is partly reduced to metallic silver, the quantity of metal thus reduced being, however, always less than that which is equivalent to the oxygen which exists in the peroxide together with baryta. The quantity reduced increases with the amount of the silver compound used, and diminishes as the temperature is higher. A small quantity of the silver-compound, or of any similar substance, is capable of decomposing a large quantity of the peroxide. Iodine, on the other hand, decomposes only an equivalent quantity, according to the equation —

$$BaO_2 + I = BaI + O_2 \text{ (Brodie*).}$$

[For the separation of oxygen from the air by first converting baryta into the peroxide, and then decomposing the latter, see p. 759.]

Peroxide of barium, heated over a large spirit-lamp in a rapid current of carbonic acid gas becomes white-hot, and at the same time small white flames burst out from its surface, probably arising from the evolution of oxygen from the still undecomposed peroxide. A similar, but much more brilliant appearance is presented when the peroxide is heated in sulphurous acid gas. (Wöhler†).

Carbonate of Baryta, mixed with carbonate of lime and charcoal, and heated to redness in a stream of aqueous vapour, is decomposed, and yields caustic baryta. This process is recommended by Jacquelain‡ for the preparation of caustic baryta.

According to Boussingault,§ a solution of chloride of barium, mixed with the native sesquicarbonate of soda called Uras, yields a precipitate of $2BaO \cdot 3CO_2$. Laurent assigns to this precipitate the formula $2BaO \cdot 3CO_2 + HO$. H. Rose,‖ on the other hand, finds that the chloride of barium and bicarbonate of soda always yield a precipitate consisting merely of $BaO \cdot CO_2$, and similarly with lime.

Recently-precipitated *sulphate of baryta*, enclosed, with a solution of bicarbonate of soda, or with dilute sulphuric acid, in a sealed glass tube, and heated for 60 hours to 250° C. (472° F.), dissolves to a slight extent, and separates out on the sides of the tube in microscopic crystals, whose form agrees with that of heavy spar. Pure water, or a solution of sulphide of sodium, does not perceptibly dissolve sulphate of baryta under similar circumstances. (Senarmont¶).

Estimation of Barium.—Barium is almost always estimated in the form of sulphate, the precipitation and filtration being performed in the manner already described for the estimation of sulphuric acid (p. 784).

Precipitation with a soluble sulphate likewise serves to separate barium from all other metals except strontium, calcium, and lead.

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* Phil. Trans. 1850, 759.

† Ann. Ch. Pharm. lxxviii. 175.

‡ Ann. Ch. Phys. [3], xxxii. 421.

§ Ibid. xxix. 397.

‖ Pogg. Ann. lxxxvi. 293.

¶ Ann. Ch. Phys. [3], xxxii. 129.

Barium is also sometimes estimated as carbonate, being precipitated by carbonate of ammonia with addition of caustic ammonia, and the liquid boiled to render the precipitation complete. The carbonate is not decomposed by ignition.

STRONTIUM.

Preparation.—This metal is also obtained by the electrolysis of its chloride in the fused state. A small crucible, with a porous cell in the middle, is filled with anhydrous chloride of strontium, mixed with a little chloride of ammonium, and in such a manner that the level of the fused chloride within the cell may be much higher than in the crucible. The negative pole placed in the cell consists of a very fine iron wire wound round a thicker one, and then covered with a piece of tobacco-pipe stem, so that only $\frac{1}{16}$th of an inch of it appears below; the positive pole is an iron cylinder, placed in the crucible round the cell. The heat should be regulated during the experiment, so that a crust may form in the cell; the metal will then collect under this crust without coming in contact with the sides of the crucible. In this manner, pieces of the metal weighing half a gramme are sometimes obtained.

Strontium resembles calcium in colour (p. 815), being only a shade darker; it oxidizes much more quickly than that metal. Its specific gravity is 2·5418. Its place in the electrical series, with water as the exciting liquid, is as follows:

$$\overset{+}{\text{K}},\quad \text{Na},\quad \text{Li},\quad \text{Ca},\quad \text{Sr},\quad \overset{-}{\text{Mg}},\quad \&c.$$

Strontium burns like calcium, and acts similarly to it when heated in chlorine, oxygen, bromine, or iodine, or on boiling sulphur, or when thrown on water or acids. (Matthiessen*).

Estimation of Strontium. — Strontium, like barium, may be estimated in the form of sulphate; but as sulphate of strontia is slightly soluble in water, it is necessary, in order to ensure complete precipitation, to add alcohol to the liquid, which may be done if there are no other substances present which are insoluble in alcohol.

Generally speaking, however, it is better to precipitate strontium in the form of a carbonate, by adding carbonate of ammonia and caustic ammonia, and heating the liquid. The precipitation of strontia in this form is more complete than that of baryta. The precipitate may be ignited on a lamp without giving off carbonic acid. It contains 59·27 per cent. of strontium, and 70·14 of strontia.

The same mode of precipitation serves to separate strontia from the alkalies.

The separation of strontia from baryta is best effected by means of hydrofluosilicic acid, which precipitates barium in the form of a crystalline silicofluoride, leaving the strontium in solution. The precipitate must be left to settle down for two or three hours; and its deposition may be accelerated by a gentle heat. It may then be collected on a weighed filter, washed with water, and dried at 100° C. The filtrate containing the strontium is then mixed with sulphuric acid, evaporated, and ignited, whereby it is converted into sulphate.

The quantities of barium and strontium in a mixture may likewise be determined by an indirect method, viz. by weighing them, first in the form of chlorides or carbonates, and afterwards as sulphates. Thus, suppose them to be first precipitated as carbonates, the united weight of which is found to be w, then converted into sulphates, the weight of which is w'. Then, to determine the quantity of baryta, x, and strontium, y, in the mixture, we have the equations

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* Chem. Soc. Qu. J. vii. 107.

$$\frac{\dot{\mathrm{Ba}}\ddot{\mathrm{C}}}{\dot{\mathrm{Ba}}}\,x + \frac{\dot{\mathrm{Sr}}\ddot{\mathrm{C}}}{\dot{\mathrm{Sr}}}\,y = w\,; \quad \frac{\dot{\mathrm{Ba}}\dddot{\mathrm{S}}}{\dot{\mathrm{Ba}}}\,x + \frac{\dot{\mathrm{Sr}}\dddot{\mathrm{S}}}{\dot{\mathrm{Sr}}} = w'\,;$$

$$\text{or, } \frac{98{\cdot}7}{76{\cdot}7}\,x + \frac{73{\cdot}7}{51{\cdot}7}\,y = w\,; \quad \frac{116{\cdot}7}{76{\cdot}7}\,x + \frac{91{\cdot}7}{51{\cdot}7}\,y = w'.$$

A similar method may be applied in all cases in which two substances in a mixture can be weighed in two distinct forms. Such methods, however, give exact results only when the quantities of the substances to be determined are not very unequal.

CALCIUM.

Preparation. — A mixture of 2 at. chloride of calcium and 1 at. chloride of strontium, with a small quantity of chloride of ammonium (this mixture being more fusible than chloride of calcium alone), is melted in a small porcelain crucible, in which a carbon positive pole is placed, while a thin harpsichord wire wound round a thicker one, and dipping only just below the surface of the melted salt, forms the negative pole. The calcium is then reduced in beads, which hang on to the fine wire, and may be separated by withdrawing the negative pole every two or three minutes, together with the small crust which forms round it. A surer method, however, of obtaining the metal, though in very small beads, is to place a pointed wire so as merely to touch the surface of the liquid; the great heat evolved, owing to the resistance of the current, causes the reduced metal to fuse and drop off from the point of the wire, and the bead is taken out of the liquid with a small iron spatula. Or, thirdly, the disposition of the apparatus may be the same as that for the reduction of strontium (p. 814).

Properties.—Calcium is a light yellow metal, of the colour of gold alloyed with silver; on a freshly cut surface, the lustre somewhat diminishes the yellow colour, which becomes more apparent when the light is reflected several times from two surfaces of calcium, or when the surface is slightly oxidized. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates having the thickness of the finest paper. Its specific gravity is 1·5778. In dry air the metal retains its colour and lustre for a few days, but in damp air the whole mass is slowly oxidized. Heated on platinum-foil over a spirit-lamp, it burns with a very bright flash. It is not quickly acted upon by dry chlorine at ordinary temperatures; but when heated, burns in that gas with a most brilliant light; also in iodine, bromine, oxygen, sulphur, &c. With phosphorus, it combines without ignition, forming phosphide of calcium. Heated mercury dissolves it as a white amalgam. Calcium rapidly decomposes water, and is still more rapidly acted on by dilute nitric, hydrochloric, and sulphuric acids, nitric acid often causing ignition. Strong nitric acid does not act upon it below the boiling heat. In the voltaic circuit, with water as the liquid element, calcium is negative to potassium and sodium, but positive to magnesium. It is not, however, reduced by potassium or sodium from its chloride by electrolysis. On the contrary, a fused mixture of CaCl with KCl or NaCl, in certain proportions, yields potassium or sodium, when subjected in a certain manner to electric action (p. 806); hence it appears that the metal formerly obtained by reducing chloride of calcium with potassium or sodium, could not be calcium, but was, probably, a mixture of potassium or sodium with aluminium, silicon, &c. (Matthiessen.*)

Lime. — According to Wittstein,† 1 part by weight of lime dissolves in 729 to 723 pts. of water, at ordinary temperatures, and in 1310 to 1569 pts. of boiling water. The carbonate of lime deposited from lime-water on exposure to the air is really the neutral carbonate, $CaO.CO_2$.

Marchand and Scheerer find that *calcspar* begins to give off carbonic acid at

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* Chem. Soc. Qu. J. viii. 28.

† Repert. Pharm. [3], i. 182.

200° C., but that a certain quantity of that acid remains with the lime, even after the most violent ignition.*

Sulphate of Lime dissolves in water containing sal-ammoniac more abundantly than in pure water, part of it appearing to be decomposed into chloride of calcium and sulphate of ammonia. The presence of nitrate of potash likewise increases the solubility of gypsum. (A. Vogel, jun.†)

Sulphate of Lime and Potash, $KO.SO_3 + CaO.SO_3 + HO$. — This salt is obtained as an accessory product in the manufacture of tartaric acid from cream of tartar. The latter salt is converted, by treatment with carbonate of lime, into tartrate of lime and neutral tartrate of potash; and by the action of sulphate of lime, all the tartaric acid is obtained in combination with lime, together with an impure solution of sulphate of potash. This solution, when evaporated, yields a hard deposit, and in slowly evaporating large quantities of it, transparent laminated crystals are obtained, having the composition expressed by the above formula; they are sparingly soluble in water, more easily in dilute hydrochloric acid. The non-crystalline deposit contains about 65 per cent. of this double salt, together with sulphate, carbonate, and phosphate of lime, carbonate of magnesia, silicate of potash, oxide of iron, alumina, water, and traces of organic matter (J. A. Phillips.‡)

Phosphate of Lime. — According to H. Ludwig,§ the precipitate produced by ordinary phosphate of soda in a solution of chloride of calcium mixed with ammonia, has, after washing and drying in the air, the composition $3CaO.PO_5 + 5\frac{1}{2}HO$; after keeping for two years in a loosely-stoppered bottle, it is reduced to $3CaO.PO_5 + 3\frac{1}{2}HO$, and of these $3\frac{1}{2}HO$, $2\frac{1}{2}$ go off below 100°. The precipitate was free from chlorine, but contained a trace of ammonia.

According to Forchhammer,‖ *apatite* may be artificially crystallized by fusing tribasic phosphate of lime, or bone-ash, with four times its weight of chloride of sodium, and leaving the fused mass to cool slowly. The mass when cold exhibits cavities containing numerous delicate six-sided prisms, having the composition of apatite.

Estimation of Calcium. — This metal may be estimated either as carbonate or as sulphate. The best method of precipitating it is, in most cases, by means of oxalate of ammonia, the oxalate being the least soluble of all the salts of calcium. If the solution contains an excess of any strong acid, such as nitric or hydrochloric acid, it must be neutralized with ammonia before adding the oxalate of ammonia, because oxalate of lime is soluble in the stronger acids. The precipitate, after being washed with hot water and dried, is heated over a lamp, care being take not to allow the heat to rise above redness. It is thereby converted into carbonate of lime, containing 40·15 p. c. of calcium and 56·12 of lime.

If, however, the solution contains any acid which forms with lime a compound insoluble in water, phosphoric or boracic acid for example, this method of precipitation cannot be adopted; because, on neutralizing with ammonia, the lime would be precipitated in combination with that acid, and would not be converted into oxalate on addition of oxalate of ammonia. In such a case, the lime may be precipitated as sulphate by adding pure dilute sulphuric acid and alcohol. The sulphate, when dried, contains 41·25 per cent. of lime. Phosphate of lime may, however, be precipitated from its acid solutions by oxalate of ammonia, with addition of acetate of ammonia, because oxalate of lime is insoluble in acetic acid, which dissolves the phosphate with facility.

From the *alkalies*, lime is easily separated either by oxalate of ammonia, or by sulphuric acid and alcohol.

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[*] J. pr. Chem. l. 237.

[†] Repert. Pharm. [3], v. 342.

[‡] Chem. Soc. Qu. J. iii. 348.

[§] Pharm. Centr. 1852, 345.

[‖] Pogg. Ann. xci. 588.

Lime is separated from *baryta* by precipitating both the earths as carbonates, dissolving the carbonates in nitric acid, evaporating to dryness, and digesting the residue in absolute alcohol, which dissolves nitrate of lime, but not nitrate of baryta. They may also be separated in this manner in the form of chlorides, but the separation is less complete, because chloride of barium is not quite insoluble in absolute alcohol.

From *strontia*, lime is separated in the same manner, nitrate of strontia being likewise insoluble in absolute alcohol.

When baryta, strontia, and lime occur together, the baryta is first separated by hydro-fluosilicic acid; the strontia and lime in the filtrate are then converted into sulphates; these sulphates, after being weighed, converted into carbonates by fusion with carbonate of soda, or by boiling with the aqueous solution of that salt (p. 736); the carbonates weighed; and the quantities of strontia and lime determined from the equations:

$$\frac{91{\cdot}7}{51{\cdot}7}x + \frac{68}{28}y = w$$

$$\frac{73{\cdot}7}{51{\cdot}7}x + \frac{50}{28}y = w';$$

in which x is the weight of strontia, y that of the lime, w that of the sulphates, and w' that of the carbonates of the two bases. Or the carbonates may be dissolved in nitric acid, and the nitrates separated by absolute alcohol.

MAGNESIUM.

Bunsen prepares this metal by the electrolysis of the fused chloride. A porcelain crucible is divided in its upper part into two halves by a vertical diaphragm (made out of a thin porcelain crucible-cover), and fitted with a cover (filed from a tile), through which the extremities of the carbon-poles of a galvanic battery are introduced into the two halves of the crucible. The crucible is then heated to redness, together with the cover and the poles; filled with fused chloride of magnesium (p. 415); and subjected to the action of a battery of 10 zinc-carbon elements. The negative pole is cut like a saw, so that the magnesium, as it separates, may lodge in the cavities, and not float on the surface of the specifically heavier liquid.* According to Matthiessen,† the metal may be much more easily obtained from a fused mixture of 4 at. chloride of magnesium and 3 at. chloride of potassium, which is prepared with more facility than the pure anhydrous chloride of magnesium. The two salts mixed in the proper proportions‡ with a little chloride of ammonium may be fused and electrolyzed in Bunsen's apparatus just described, the cutting of the negative pole being, however, dispensed with, as the metal is heavier than the fused mixture. A very simple and convenient way of reducing the metal, especially for the lecture-table, is to fuse the mixture in a common clay tobacco-pipe over an argand spirit-lamp or gas-burner, the negative pole being an iron wire passed up the pipe-stem, and the positive a piece of gas-coke, just touching the surface of the fused chlorides. (Matthiessen.)

Magnesium may, however, be obtained in much larger quantity, by heating a mixture of 600 grammes of chloride of magnesium, 100 grms. fused chloride of sodium, and 100 grms. of pulverized fluoride of calcium, with 100 grms. of sodium, to bright redness, in a covered earthen crucible. The magnesium is thereby obtained in globules, which are afterwards heated nearly to whiteness in a boat of compact charcoal, placed within an inclined tube of the same material, through which a stream of dry hydrogen is passed. The magnesium then vola-

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* Ann. Ch. Pharm. 82, 137.

† Chem. Soc. Qu. J. viii. 107.

‡ The solution of the chloride of magnesium may be evaporated almost to dryness, and analyzed to find the proportion of anhydrous salt present.

tilizes and condenses in the upper part of the tube. Lastly, it is remelted with a flux composed of chloride of magnesium, chloride of sodium, and fluoride of calcium, and is thus obtained in large globules. (H. Deville and Caron.)*

Magnesium on the recently-fractured surface is sometimes slightly crystalline and coarsely laminated; sometimes fine-grained. In the former cases it is silver-white and shining; in the latter, bluish grey and dull. Its specific gravity is 1·7430 at + 5° C. (Bunsen): 1·75, according to Deville and Caron. It is about as hard as calcspar, and may be easily filed, bored, sawn, and flattened to a certain extent, but is scarcely more ductile than zinc at ordinary temperatures. It melts at a moderate red heat (Bunsen); melts and volatilizes at about the same temperature as zinc (Deville and Caron). It does not alter in a dry atmosphere, but in damp air soon becomes covered with a film of hydrate of magnesia. Heated to redness in the air, or in oxygen gas, it burns with a dazzling white light, and forms magnesia. It decomposes pure cold water but slowly, acidulated water very quickly; when thrown on aqueous hydrochloric acid, it takes fire momentarily; strong sulphuric acid dissolves it but slowly; a mixture of sulphuric acid and fuming nitric acid does not act upon it at ordinary temperatures. It burns when heated in chlorine gas; also in bromine-vapour, though with less facility; in sulphur and iodine-vapour very brilliantly (Bunsen).

Estimation of Magnesium. — When magnesia occurs in a solution not containing any other fixed substance, its quantity may be determined by evaporating to dryness, igniting the residue, then moistening it with sulphuric acid slightly diluted with water, and expelling the excess of that acid at a low red heat; sulphate of magnesia then remains, containing 33·7 per cent. of magnesia.

If the solution contains other fixed substances, the magnesia must be precipitated by the addition of ammonia in excess and phosphate of soda. The precipitated ammonio-magnesian phosphate is then treated in the manner described at p. 790. The pyrophosphate of magnesia obtained by igniting it contains 36·33 per cent. of magnesia.

From *baryta* and *strontia*, magnesia is separated by sulphuric acid; from lime, by oxalate of ammonia, with addition of chloride of ammonium to prevent the precipitation of the magnesia.

From the *alkalies*, magnesia may be separated by converting the bases into sulphates, and adding baryta-water. The magnesia is then precipitated in the form of hydrate, together with sulphate of baryta. The precipitate, after washing, is digested with dilute sulphuric acid, which extracts the magnesia in the form of sulphate; and the filtrate containing the alkalies, together with the excess of baryta, is also treated with sulphuric acid, which precipitates the baryta, and converts the alkalies into sulphates.

ALUMINIUM, OR ALUMINUM.

Preparation. — This metal is now obtained in considerable quantity by decomposing the chloride or fluoride with sodium. The chloride of aluminium is prepared on the large scale by passing chlorine over a previously ignited mixture of clay and coal-tar in retorts like those used in the preparation of coal-gas, and is either made to pass into a chamber lined with plates of earthenware, where it condenses into a compact crystalline mass; or the vapour is made to pass over chloride of sodium at a red heat, whereby it is converted into the double chloride of aluminium and sodium. To effect the reduction, 400 pts. of this double salt, 200 pts. of chloride of sodium, 200 pts. of fluor-spar (or better, of cryolite), all perfectly dry and finely pounded, are mixed together, and the mixture placed, together with 75 or 80 parts of sodium, in an earthern crucible, the saline mixture

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* Ann. Ch. Pharm. ci. 359.

and the sodium being deposited in alternate layers. The crucible is then moderately heated till the action begins, afterwards to redness, the melted mass stirred with an earthenware rod, and afterwards poured out. Twenty parts of aluminium are thus obtained in a compact lump, and about 5 parts in globules encrusted with a grey mass. (H. Ste-Claire Deville.)*

Aluminium may also be prepared in a similar manner from cryolite, the native fluoride of aluminium and sodium, which is now imported in large quantities from Greenland. (H. Rose.)† Instead of this natural mineral, an artificial cryolite may be used, prepared by mixing 1 part of burnt clay with 3 parts, or rather more, of anhydrous carbonate of soda, supersaturating the mixture with hydrofluoric acid, then drying and fusing it at a red heat. A fluoride of aluminium and potassium possessing analogous properties may be prepared by a similar process. (Deville.)‡

Aluminium may likewise be obtained by the electrolysis of the double chloride of aluminium and sodium, the process being similar to that adopted by Bunsen for the electrolysis of chloride of magnesium. (Deville, Bunsen.)

Pure aluminium is a white metal, with a faint bluish iridescence; when recently fused, it is soft like pure silver, and has a density of 2.56; but after hammering or rolling, it is as hard as iron, and has a density of 2.67. A bar of it is very sonorous. It conducts electricity eight times as well as iron, and is slightly magnetic. Its melting point is between those of zinc and silver: when solidified from fusion, or reduced by electrolysis, it exhibits crystalline forms, apparently regular octohedrons. It does not oxidize in the air, even at a strong red heat; neither does it decompose water, excepting at the strongest red heat,—and even then but slowly. It does not dissolve in nitric acid, either dilute or concentrated, at ordinary temperatures, and but very slowly in boiling nitric acid; dilute sulphuric acid scarcely attacks it at ordinary temperatures, even after a long time; but hydrochloric acid, at any degree of concentration, dissolves it readily, even at low temperatures, with evolution of hydrogen. It is not attacked by hydrosulphuric acid, or by the fused hydrates of the alkalies. It does not combine with mercury, and when fused with lead, takes up only traces of that metal. With copper it unites in various proportions, forming light, very hard, white alloys, and it combines also with silver and iron. (Deville.)

Alumina.—The specific gravity of alumina ignited over a spirit-lamp is from 3.87 to 3.90; after 6 hours' ignition in an air-furnace, 3.75 to 3.725; and after ignition in a porcelain furnace, 3.999, which agrees very nearly with that of naturally crystallized alumina as it occurs in the ruby, sapphire, and corundum. (H. Rose.§)

Bihydrate of Alumina, soluble in water, $Al_2O_3 + 2HO$. When a dilute solution of biacetate of alumina (see page 820), is exposed to heat for several days, the whole of the acetic acid appears to become free, and the alumina passes into an allotropic state in which it is *soluble in water*, and is no longer capable of acting as a mordant, or of entering into any definite combination. This allotropic alumina retains 2 at. water when dried at 100° C. Its solution is coagulated by mineral acids and by most vegetable acids, by alkalies, by a great number of neutral salts, and by decoctions of dye-woods. It is insoluble in the stronger acids, but soluble in acetic acid, unless it has been previously coagulated in the manner just mentioned. Boiling potash changes it into the ordinary terhydrate. Its coagulum with dye-woods has the colour of the infusion, but is translucent, and entirely different from the dense opaque cakes which ordinary alumina forms with the same colouring matters. (Walter Crum.||)

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* Ann. Ch. Phys. [3], xlvi. 415; see also Compt. rend. xxxviii. 279; xl. 1298.

† Pogg. Ann. xcvi. 152.

‡ Ann. Ch. Phys. [3], xlix. 83.

§ Pogg. Ann. lxxiv. 430.

|| Chem. Soc. Qu. J. vii. 225.

According to Phillips,* hydrate of alumina when kept after precipitation in a moist atmosphere, or under water, becomes after a few days difficult to dissolve in acids.

Alum.—By fusing ignited alumina with four times its weight of bisulphate of potash, a mass is obtained, which when treated with warm water, leaves an insoluble residue, consisting of thin microscopic six-sided tables, which refract light singly. They contain 23 per cent. potash, 30.7 sulphuric acid, and 46.3 alumina, and appear to consist of crystallized anhydrous alum. (Salm-Horstmar.†)

Nitrate of Alumina.—According to Ordway,‡ a concentrated and somewhat acid solution of alumina in nitric acid, deposits colourless, flattened, oblique rhombic prisms, containing $Al_2O_3 . 3NO_5 + 18HO$. These crystals melt at 72.8° C. into a colourless liquid which solidifies in the crystalline form on cooling; they are deliquescent, and dissolve in water and in nitric acid. Half an ounce of the pulverized crystals mixed with an equal weight of bicarbonate of ammonia, lowered the temperature from 10.5° to —23.3° C. By the action of this salt upon hydrate of alumina, basic salts appear to be formed. Salm-Horstmar,§ by evaporating and cooling a solution of hydrate of alumina in nitric acid of 26.3 per cent., likewise obtained a salt which crystallized in rhombic prisms and (by truncation) in hexagonal tables; but after repeated solution in water, it no longer crystallized distinctly; and its aqueous solution was decomposed by evaporation at a somewhat elevated temperature.

Acetates of Alumina.—By decomposing tersulphate of alumina (p. 421), with neutral acetate of lead, a solution is formed, consisting apparently of a mixture of biacetate of alumina with 1 at. free acetic acid.

When this aluminous solution is evaporated at a low temperature and with sufficient rapidity,—as by spreading the concentrated solution very thinly over sheets of glass or porcelain, exposing it to a temperature not exceeding 100° F., and, as it runs together in drops, rubbing it constantly with a platinum or silver spatula,—a dry substance is obtained which may be redissolved easily and entirely by water. This is the biacetate of alumina, $Al_2O_3 . 2C_4H_3O_3 + 4HO$: the alumina contained in it retains all its usual properties.

When the first aluminous solution, containing not less than 4 or 5 per cent. of alumina, is left for some days in the cold, a salt is deposited in the form of a white crust, which is an *allotropic biacetate of alumina insoluble in water.* Heat effects the same change in the aluminous solution more rapidly, and the insoluble biacetate then separates in the form of a granular powder. At the boiling temperature, the liquid is thus deprived, in half an hour, of the whole of its alumina, which goes down with $\frac{2}{3}$ of the acetic acid, leaving $\frac{1}{3}$ in the liquid.

The soluble biacetate of alumina is decomposed by heat, yielding the bihydrate of alumina soluble in water already described (p. 820). The insoluble biacetate of alumina, when digested in a large quantity of water, is gradually changed into the soluble biacetate, part of which, however, is decomposed during the process into acetic acid and the allotropic bihydrate of alumina.

The precipitate which is formed on the application of heat to a mixed solution of acetate of alumina and sulphate of potash, and which is soluble in cold acetic acid, is a bibasic sulphate of alumina, $2Al_2O_3 . SO_3 + 10HO$.

Common salt added to a solution of teracetate of alumina forms, on the application of heat, a very finely divided white precipitate, containing 44·66 per cent. alumina, 21·96 acetic acid, 5·51 hydrochloric acid, 25·90 water, and 1·97 chloride of sodium. A similar precipitate is formed by nitrate of potash (Walter Crum.‖)

Estimation of Alumina.—Alumina is precipitated from its solutions in the form of hydrate by ammonia, carbonate of ammonia, or sulphide of ammonium;

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* Chem. Gaz. 1848, 349.

† J. pr. Chem. lii. 319.

‡ Sill. Am. J. [2], ix. 30.

§ J. pr. Chem. lix. 208.

‖ Chem. Soc. Qu. J. vii. 217.

the precipitate when ignited yields pure anhydrous alumina, containing 53·26 per cent. of the metal.

Precipitation with ammonia or sulphide of ammonium serves also to separate alumina from the preceding bases. In thus separating it from the alkaline earths, care must be taken not to expose the liquid to the air; otherwise carbonic acid will be absorbed by the excess of ammonia, and the alkaline earths precipitated as carbonates. From baryta, alumina is most readily separated by sulphuric acid.

GLUCINUM.

This metal and its compounds have been minutely examined by Debray.* The metal may be obtained from the chloride by reduction with sodium. It is a white metal, whose density is 2·1. It may be forged, and rolled into sheets like gold. Its melting-point is below that of silver. It may be melted in the outer blowpipe-flame, without exhibiting the phenomenon of ignition presented by zinc and iron under the same circumstances; it cannot even be set on fire in an atmosphere of pure oxygen, but in both experiments becomes covered with a thin coat of oxide, which seems to protect it from further change. It does not appear to combine with sulphur under any circumstances, but unites directly with chlorine and iodine with the aid of heat. Silicon unites readily with glucinum, forming a hard brittle substance susceptible of a high polish; this alloy is always formed when glucinum is reduced in porcelain vessels. Glucinum does not decompose water at a boiling heat, or even when heated to whiteness. Sulphuric and hydrochloric acid dissolve it, with evolution of hydrogen. Nitric acid, even when concentrated, does not act upon it at ordinary temperatures, and dissolves it but slowly at a boiling heat. Glucinum is not attacked by ammonia, but dissolves readily in caustic potash.

The above-mentioned properties differ considerably from those of the metal which Wöhler obtained by igniting chloride of glucinum with potassium in a platinum crucible; the metal thus obtained being a grey powder, very refractory in the fire, but combining with oxygen, sulphur, and chlorine much more energetically than Debray's metal. The differences appear to be due, partly to the different states of aggregation, and partly to the contamination of Wöhler's metal with platinum and potassium.

Glucina.—Debray prepares this earth from the emerald of Limoges by the following process. The mineral, finely pounded (levigation with water is quite superfluous), is fused with half its weight of quicklime in an air-furnace, and the glass thus obtained is treated, first with dilute, and then with strong nitric acid, till it is reduced to a homogeneous jelly. The product is then evaporated to dryness, and heated sufficiently to decompose the nitrates of alumina, glucina, and iron, and a small portion of the nitrate of lime; and the residue, consisting of silica, alumina, glucina, sesquioxide of iron, nitrate of lime, and a small quantity of free lime, is boiled with water containing sal-ammoniac, which dissolves the nitrate of lime immediately, and the free lime after a while, with evolution of ammonia. (If no ammonia is evolved, the calcination has not been carried far enough and must be repeated.) The liquid is then decanted; the precipitate, after thorough washing, treated with boiling nitric acid; and the resulting solution of alumina, glucina, and iron poured into a solution of carbonate of ammonia mixed with free ammonia. The earths are thereby precipitated without evolution of carbonic acid, and the glucina redissolves, after seven or eight days, in the excess of carbonate of ammonia. As the carbonate of ammonia may also dissolve a small quantity of iron, it should be mixed with a little sulphide of ammonium to precipitate the iron completely. Lastly, the carbonate of ammonia is distilled off, and the carbonate of glucina which remains yields pure glucina by calcination.

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* Ann. Ch. Phys. [3], xliv. 5.

Glucina is not hardened by heat like alumina, but merely rendered less soluble in acids. Ebelmen has obtained it in hexagonal prisms by exposing a solution of glucina in fused boracic acid to a powerful and long-continued heat. It may be more easily obtained in microscopic crystals, apparently of the same form, by decomposing the sulphate at a high temperature in presence of sulphate of potash, also by calcining the double carbonate of glucina and ammonia.

Hydrate of glucina dissolves in potash like alumina, but is reprecipitated by boiling when the solution is diluted with water to a certain extent. It is likewise soluble in carbonate of potash or soda, sulphurous acid, and bisulphite of ammonia. When precipitated by ammonia, especially from the oxalate or acetate, it is completely redissolved by prolonged ebullition.

Glucina was regarded by Berzelius as a sesquioxide, Gl_2O_3, while Awdejew and others regard it as a protoxide, GlO. The latter formula appears preferable, first because it gives more simple formulæ for the salts of glucina than the former, and secondly, because glucina, on the whole, exhibits a closer resemblance to known protoxides, such as magnesia, than to sesquioxides, such as alumina. The greater simplicity of the formulæ derived from the formula GlO, will be seen from the following table:

Neutral sulphate of glucina................	$GlO.SO_3 + 4HO$ or $Gl_2O_3.SO_3 + 12HO$.
Sulphate of glucina and potash...........	$KO.SO_3 + GlO.SO_3 + 3HO$ or $3(KO.SO_3) + Gl_2O_3.3SO_3 + 6HO$.
Carbonate of glucina and ammonia......	$3(NH_4O.CO_2) + 4GlO.3CO_2 + HO$ or $9(NH_4O.CO_2) + 4Gl_2O_3.9CO_2 + 3HO$.
Oxalate of glucina and potash............	$KO.C_2O_3 + GlO_2C_2O_3$ or $3(KO.C_2O_3) + Gl_2O_3.3C_2O_3$.

The reasons which induced Berzelius to regard glucina as a sesquioxide, were founded on the resemblance of glucina and alumina in the hydrated state, from the volatility of the chlorides, and from the supposed capability of glucina and alumina to replace one another in minerals, as in cymophane and in emerald. This last point has been completely settled by the researches of Awdejew and of Damour, from which it appears that cymophane, the native aluminate of glucina, has always the same composition ($GlO.Al_2O_3$), from whatever locality it may be derived. With regard to the hydrates, it is true that alumina and glucina are precipitated under the same circumstances; but there the resemblance ends. Glucina, when dried in the air, absorbs carbonic acid and forms a carbonate, which alumina does not. The existence of a definitely crystallized carbonate of ammonia and glucina (obtained by boiling a solution of glucina in carbonate of ammonia, stopping the ebullition as soon as turbidity appears, then filtering, and adding alcohol) constitutes another important difference between that earth and alumina. The anhydrous oxides likewise differ essentially. Glucina volatilizes, like magnesia, without melting, whereas alumina fuses under the same circumstances. Glucina cannot be fused with lime, like alumina, the presence of another body, such as silica or alumina, being required to enable the fusion to take place. In this respect again glucina resembles magnesia. The identity of crystalline form which has been observed between glucina and alumina is merely an isolated fact, which would be important if the two bodies possessed similar chemical properties, but not otherwise.

Chloride of glucinum exhibits at first sight considerable resemblance to chloride of aluminium, and is prepared in a similar manner; but the resemblance does not go far. Chloride of glucinum is less volatile than chloride of aluminium: thus, when a mixture of finely powdered emerald and charcoal, made into a paste with oil, is calcined in a crucible, then powdered, and heated in a porcelain tube through which chlorine gas is passed, chloride of glucinum and chloride of aluminium are formed together; but the chloride of glucinum passes over first, and may be separately condensed. Chloride of glucinum is, in fact, about as volatile as chloride of zinc. Chloride of aluminium unites with the alkaline chlorides, forming compounds which may be called *spinelles*, and are represented by the general formula MCl + Al_2Cl_3; but chloride of glucinum does not form any similar compound.

It must, however, be remembered that glucina does not exhibit any very close analogy to the class of protoxides. It is not isomorphous with lime or magnesia. Cymophane may be represented by the general formula of the spinelles, $GlO.Al_2O_3$; but the dissimilarity of its crystalline form prevents it from being included in that class of minerals. The emerald also differs completely in crystalline form from the generality of silicates of the same composition, whose general formula is $MO.SiO_3 + M_2'O_3.3SiO_3$. Neither is there any greater analogy between the double sulphates, carbonates, and oxalates of glucina and those of lime or magnesia. On the whole, glucina appears to be intermediate in its properties between the protoxides and sesquioxides.

Glucina is precipitated from its solutions for quantitative analysis in the same manner as alumina. From the latter it is separated by carbonate of ammonia.

TABLE A.

FOR CONVERTING FRENCH DECIMAL MEASURES AND WEIGHTS INTO ENGLISH MEASURES AND WEIGHTS.

1 Meter = 1·0936331 English yards.
= 3·2808992 " feet.
= 39·37079 " inches.

1 Liter = 0·2209687 Imperial gallons.
= 1·7677496 " pints.
= 0·35317 cubic feet.
= 61·02710 " inches.

1 Kilogramme = 0·0196969 cwt.
= 2·20606 lb. (avoird.)
= 2·68098 lb. (troy.)

1 Gramme = 15·44242 grains.

These values are taken from the "Table of Constants" at the end of the Tables of Logarithms published by the Society for the Diffusion of Useful Knowledge.

The Imperial Gallon is equal to 277·24 cubic inches, and contains 10 lbs. avoirdupois of water at 60° Fah.

TABLE B.

BAROMETER SCALE IN MILLIMETERS AND INCHES.

Mm.	In.	Mm.	In.	Mm.	In.
700	27·560	730	28·741	760	29·922
701	27·599	731	28·780	761	29·962
702	27·639	732	28·820	762	30·001
703	27·678	733	28·859	763	30·040
704	27·717	734	28·899	764	30·080
705	27·756	735	28·938	765	30·119
706	27·795	736	28·977	766	30·159
707	27·835	737	29·017	767	30·198
708	27·875	738	29·056	768	30·237
709	27·914	739	29·096	769	30·277
710	27·954	740	29·135	770	30·316
711	27·993	741	29·174	771	30·355
712	28·032	742	29·214	772	30·395
713	28·072	743	29·253	773	30·434
714	28·111	744	29·292	774	30·474
715	28·151	745	29·332	775	30·513
716	28·190	746	29·371	776	30·552
717	28·229	747	29·411	777	30·592
718	28·269	748	29·450	778	30·631
719	28·308	749	29·489	779	30·671
720	28·347	750	29·529	780	30·710
721	28·387	751	29·568	781	30·749
722	28·426	752	29·607	782	30·788
723	28·466	753	29·647	783	30·828
724	28·505	754	29·686	784	30·867
725	28·544	755	29·725	785	30·907
726	28·584	756	29·765	786	30·946
727	28·623	757	29·804	787	30·985
728	28·662	758	29·844	788	31·025
729	28·702	759	29·882	789	31·064

28 inches = 711·187 millimeters.
29 " = 736·587 "
30 " = 761·986 "
31 " = 787·386 "

1 millimeter = 0·03937079 inch. | 1 inch = 25·39954 millimeters.

TABLE C.

FOR CONVERTING DEGREES OF THE CENTIGRADE THERMOMETER INTO DEGREES OF FAHRENHEIT'S SCALE.

Cent.		Fah.	Cent.		Fah.	Cent.		Fah.
— 100°	...	— 148·0°	— 44°	...	— 47·2°	+ 12°	...	+ 53·6°
99	...	146·2	43	...	45·4	13	...	55·4
98	...	144·4	42	...	43·6	14	...	57·2
97	...	142·6	41	...	41·8	15	...	59·0
96	...	140·8	40	...	40·0	16	...	60·8
95	...	139·0	39	...	38·2	17	..	62·6
94	...	137·2	38	...	36·4	18	...	64·4
93	...	135·4	37	...	34·6	19	...	66·2
92	...	133·6	36	...	32·8	20	...	68·0
91	...	131·8	35	...	31·0	21	...	69.8
90	...	130·0	34	...	29·2	22	...	71·6
89	...	128·2	33	...	27·4	23	...	73·4
88	...	126·4	32	...	25·6	24	...	75·2
87	...	124·6	31	...	23·8	25	...	77·0
86	...	122·8	30	...	22·0	26	...	78·8
85	...	121·0	29	...	20·2	27	...	80·6
84	...	119·2	28	...	18·4	28	...	82·4
83	...	117·4	27	...	16·6	29	...	84·2
82	...	115 6	26	...	14·8	30	...	86·0
81	...	113·8	25	...	13·0	31	...	87·8
80	...	112·0	24	...	11·2	32	...	89·6
79	...	110·2	23	...	9·4	33	...	91·4
78	...	108·4	22	...	7·6	34	...	93·2
77	...	106·6	21	...	5·8	35	...	95·0
76	...	104·8	20	...	4·0	36	...	96·8
75	...	103·0	19	...	2·2	37	...	98·6
74	...	101·2	18	...	0·4	38	...	100·4
73	...	99·4	17	...	+ 1·4	39	...	102.1
72	...	97·6	16	...	3·2	40	...	104·0
71	...	95·8	15	...	5·0	41	...	105·8
70	...	94·0	14	...	6·8	42	...	107·6
69	...	92·2	13	...	8·6	43	...	109·4
68	...	90·4	12	...	10·4	44	...	111·2
67	...	88·6	11	...	12·2	45	...	113·0
66	...	86·8	10	...	14·0	46	...	114·8
65	...	85·0	9	...	15·8	47	...	116·6
64	...	83·2	8	...	17·6	48	...	118·4
63	...	81·4	7	...	19·4	49	...	120.2
62	...	79·6	6	...	21·2	50	...	122·0
61	...	77·8	5	...	23·0	51	...	123·8
60	...	76·0	4	...	24·8	52	...	125·6
59	...	74·2	3	...	26·6	53	...	127·4
58	...	72·4	2	...	28·4	54	...	129·2
57	..	70·6	1	...	30·2	55	...	131·0
56	.	68·8	0	...	32·0	56	...	132·8
55	...	67·0	+ 1	...	33·8	57	...	134·6
54	...	65·2	2	...	35·6	58	...	136·4
53	...	63·4	3	...	37·4	59	...	138·2
52	...	61·6	4	...	39·2	60	...	140·0
51	...	59·8	5	...	41·0	61	...	141·8
50	...	58·0	6	...	42·8	62	...	143·6
49	...	56·2	7	...	44·6	63	...	145.4
48	...	54·4	8	...	46·4	64	...	147·2
47	...	52·6	9	...	48·2	65	...	149·0
46	...	50·8	10	...	50·0	66	...	150·8
45	...	49·0	11	...	51·8	67	...	152·6

TABLE C.—(*continued.*)

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
+ 68°	+ 154·4°	+ 130°	+ 266·0°	+ 192°	+ 377·6°
69	156·2	131	267·8	193	379·4
70	158·0	132	269·6	194	381·2
71	159·8	133	271·4	195	383·0
72	161·6	134	273·2	196	384·8
73	163·4	135	275·0	197	386·6
74	165·2	136	276·8	198	388·4
75	167·0	137	278·6	199	390·2
76	168·8	138	280.4	200	392·0
77	170·6	139	282·2	201	393·8
78	172·4	140	284·0	202	395·6
79	174·2	141	285·8	203	397·4
80	176·0	142	287·6	204	399·2
81	177·8	143	289·4	205	401·0
82	179 6	144	291·2	206	402·8
83	181·4	145	293·0	207	404·6
84	183·2	146	294·8	208	406·4
85	185·0	147	296·6	209	408·2
86	186·8	148	298·4	210	410·0
87	188·6	149	300·2	211	411·8
88	190·4	150	302·0	212	413·6
89	192·2	151	303·8	213	415·4
90	194·0	152	305·6	214	417·2
91	195·8	153	307·4	215	419·0
92	197·6	154	309·2	216	420·8
93	199·4	155	311·0	217	422·6
94	201·2	156	312·8	218	424·4
95	203·0	157	314·6	219	426·2
96	204·8	158	316·4	220	428·0
97	206·6	159	318·2	221	429·8
98	208·4	160	320·0	222	431·6
99	210·2	161	321·8	223	433·4
100	212·0	162	323·6	224	435·2
101	213·8	163	325·4	225	437·0
102	215·6	164	327·2	226	438·8
103	217·4	165	329·0	227	440·6
104	219·2	166	330·8	228	442·4
105	221·0	167	332·6	229	444·2
106	222·8	168	334·4	230	446·0
107	224·6	169	336·2	231	447·8
108	226·4	170	338·0	232	449·6
109	228·2	171	339·8	233	451·4
110	230·0	172	341·6	234	453·2
111	231·8	173	343·4	235	455·0
112	233·6	174	345·2	236	456·8
113	235·4	175	347·0	237	458·6
114	237·2	176	348·8	238	460·4
115	239·0	177	350·6	239	462·2
116	240·8	178	352·4	240	464·0
117	242·6	179	354·2	241	465·8
118	244·4	180	356·0	242	467·6
119	246·2	181	357·8	243	469·4
120	248·0	182	359·6	244	471·2
121	249·8	183	361·4	245	473·0
122	251·6	184	363·2	246	474·8
123	253·4	185	365·0	247	476·6
124	255·2	186	366·8	248	478·4
125	257·0	187	368·6	249	480·2
126	258·8	188	370·4	250	482·0
127	260·6	189	372·2	251	483·8
128	262·4	190	374·0	252	485·6
129	264·2	191	375·8	253	487·4

TABLE C.—(*continued.*)

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
+ 254°	+ 489·2°	+ 286°	+ 546·8°	+ 318°	+ 604·4°
255	491·0	287	548·6	319	606·2
256	492·8	288	550·4	320	608·0
257	494·6	289	552·2	321	609·8
258	496·4	290	554·0	322	611·6
259	498·2	291	555·8	323	613·4
260	500·0	292	557·6	324	615·2
261	501·8	293	559·4	325	617·0
262	503·6	294	561·2	326	618·8
263	505·4	295	563·0	327	620·6
264	507·2	296	564·8	328	622·4
265	509·0	297	566·6	329	624·2
266	510·8	298	568·4	330	626·0
267	512·6	299	570·2	331	627·8
268	514·4	300	572·0	332	629·6
269	516·2	301	573·8	333	631·4
270	518·0	302	575·6	334	633·2
271	519·8	303	577·4	335	635·0
272	521·6	304	579·2	336	636·8
273	523·4	305	581·0	337	638·6
274	525·2	306	582·8	338	640·4
275	527·0	307	584·6	339	642·2
276	528·8	308	586·4	340	644·0
277	530·6	309	588·2	341	645·8
278	532·4	310	590·0	342	647·6
279	534·2	311	591·8	343	649·4
280	536·0	312	593·6	344	651·2
281	537·8	313	595·4	345	653·0
282	539·6	314	597·2	346	654·8
283	541·4	315	599·0	347	656·6
284	543·2	316	600·8	348	658·4
285	545·0	317	602·6	349	660·2

TABLE D.

COMPARISON OF THE DEGREES OF BAUMÉ'S HYDROMETER WITH THE REAL SPECIFIC GRAVITIES.

1. *For Liquids heavier than Water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	20	1·152	39	1·345	58	1·617
1	1·007	21	1·160	40	1·357	59	1·634
2	1·013	22	1·169	41	1·369	60	1·652
3	1·020	23	1·178	42	1·381	61	1·670
4	1·027	24	1·188	43	1·395	62	1·689
5	1·034	25	1·197	44	1·407	63	1·708
6	1·041	26	1·206	45	1·420	64	1·727
7	1·048	27	1·216	46	1·434	65	1·747
8	1·056	28	1·225	47	1·448	66	1·767
9	1.063	29	1·235	48	1·462	67	1·788
10	1.070	30	1·245	49	1·476	68	1·809
11	1·078	31	1·256	50	1·490	69	1·831
12	1·085	32	1·267	51	1·495	70	1·854
13	1·094	33	1·277	52	1·520	71	1·877
14	1·101	34	1·288	53	1·535	72	1·900
15	1·109	35	1·299	54	1·551	73	1·924
16	1·118	36	1·310	55	1·567	74	1·949
17	1·126	37	1·321	56	1·583	75	1·974
18	1·134	38	1·333	57	1·600	76	2·000
19	1·143						

TABLE D.—(*continued.*)

2. *Baumé's Hydrometer for Liquids lighter than Water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794		

Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water.

In the United Kingdom, Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real specific gravity can be deduced by an extremely simple method from the degree of the hydrometer, namely, by multiplying the latter by 5, and adding 1000; the sum is the specific gravity, water being 1000. Thus 10° Twaddell indicates a specific gravity of 1050°, or 1·05; 90° Twaddell, 1450, or 1·45.

TABLE E.

SHOWING THE PROPORTION BY WEIGHT, OF ABSOLUTE OR REAL ALCOHOL, IN 100 PARTS OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES. (FOWNES.)

Sp. Gr. at 60° F.	Percentage of real Alcohol.	Sp. Gr. at 60° F.	Percentage of real Alcohol.	Sp. Gr. at 60° F.	Percentage of real Alcohol.	Sp. Gr. at 60° F.	Percentage of real Alcohol.
·9991	0·5	·9638	26	·9160	51	·8581	76
·9981	1	·9623	27	·9135	52	·8557	77
·9965	2	·9609	28	·9113	53	·8533	78
·9947	3	·9593	29	·9090	54	·8508	79
·9930	4	·9578	30	·9069	55	·8483	80
·9914	5	·9560	31	·9047	56	·8459	81
·9898	6	·9544	32	·9025	57	·8434	82
·9884	7	·9528	33	·9001	58	·8408	83
·9869	8	·9511	34	·8979	59	·8382	84
·9855	9	·9490	35	·8956	60	·8357	85
·9841	10	·9470	36	·8932	61	·8331	86
·9828	11	·9452	37	·8908	62	·8305	87
·9815	12	·9434	38	·8886	63	·8279	88
·9802	13	·9416	39	·8863	64	·8254	89
·9789	14	·9396	40	·8840	65	·8228	90
·9778	15	·9376	41	·8816	66	·8199	91
·9766	16	·9356	42	·8793	67	·8172	92
·9753	17	·9335	43	·8769	68	·8145	93
·9741	18	·9314	44	·8745	69	·8118	94
·9728	19	·9292	45	·8721	70	·8089	95
·9716	20	·9270	46	·8696	71	·8061	96
·9704	21	·9249	47	·8672	72	·8031	97
·9691	22	·9228	48	·8649	73	·8001	98
·9678	23	·9206	49	·8625	74	.7969	99
·9665	24	·9184	50	·8603	75	·7938	100
·9652	25						

INDEX.

THE END.