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From *The Saturday Review*

"A well-written, clear and accurate Elementary Manual of Inorganic Chemistry. . . . We agree heartily in the system adopted by Drs. Dupré and Hake. Will make Experimental Work trebly interesting because intelligible."

LONDON: CHARLES GRIFFIN & COMPANY, LIMITED.

A SHORT MANUAL

OF

INORGANIC CHEMISTRY.

BY

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Second Edition, Revised.

LONDON:
CHARLES GRIFFIN & COMPANY, LIMITED,
EXETER STREET, STRAND.
1892.

This Work is Dedicated by the Authors

TO

DR. HEINRICH WILL,

RITTER ERSTER CLASSE DES GROSSHERZOGLICH HESSISCHEN LUDWIGSORDENS
UND DES ORDENS PHILIPPS DES GROSSMÜTHIGEN; MITGLIED
DER AKADEMIE DER WISSENSCHAFTEN IN MÜNCHEN,
MADRID, UND TURIN;
FOREIGN MEMBER OF THE CHEMICAL SOCIETY OF LONDON;
LATE PROFESSOR OF CHEMISTRY IN THE
UNIVERSITY OF GIESSEN;

In Grateful Remembrance of
His Teaching.

PREFACE TO THE SECOND EDITION.

It is with much pleasure that we issue a Second Edition of our "Manual of Inorganic Chemistry," since, notwithstanding the multiplicity of text-books on this subject, our anticipation that there was still room for another has been fully justified.

In preparing the new edition, we have strictly adhered to the systematic method originally laid down—a method which specially appears to have found favour at the hands of our critics.

Since the appearance of the first edition many important observations have been made in this branch of Chemistry, to which many able Chemists are again devoting their attention. We have endeavoured to bring the statement of facts up to date without increasing the bulk of the work, and to remove those errors incidental to a first edition to which our attention has been drawn.

We take this opportunity of thanking many scientific friends for some valuable suggestions and for their kindly appreciation of our efforts.

A. DUPRÉ.
H. WILSON HAKE.

Westminster Hospital Medical School,
Caxton Street, S.W., *Sept.*, 1892.

PREFACE TO THE FIRST EDITION.

THE appearance of a new Manual of Chemistry may give rise in the minds of some Chemists to the question :—Why should another handbook on this subject be added to the many which already exist in the language?

In anticipation of this question, we may state, firstly, that we claim the right of a somewhat lengthened experience as teachers to record our own methods of instruction; and that, secondly, we believe that the very multiplicity of text-books already published tends to show a want felt, but not yet satisfied.

As regards method, we are strongly of opinion that general principles should precede what may be termed descriptive Chemistry; and we have, therefore, given them precedence in this work. We have found such an arrangement advantageous in teaching, for the following reasons, viz., general principles can be clearly comprehended by a student who has no previous knowledge of Chemistry whatever, but the description of the simplest phenomenon connected with the chemical properties or preparation of any substance, cannot be understood in its entirety in the absence of a knowledge of general principles.

It is assumed by us in this work, that the reader has no previous knowledge of Chemistry whatever; therefore, in laying down general principles in the introductory portion, we have proceeded step by step, and have avoided, as far as possible, the supposition that the student is in possession of any information not already imparted by us. In other words, we abstain from referring forward, except in a few instances which do not affect the general plan.

The Introduction is intended to be read straight through, and in the descriptive portion of the work which follows, it is further assumed that this introductory portion has been previously mastered.

In the descriptive portion, we have adopted, as far as was possible, a uniform arrangement of the many facts relating to the properties of each element or compound, in order to facilitate their more ready acquisition; the general outlines of this arrangement are tabulated at the end of the Introduction (p. 83).

This systematic arrangement of facts will, we venture to hope, also render the book more valuable as a work of reference than is usually the case with a smaller treatise.

We have also given very briefly the prominent facts relating to the *physiological action* of the more important elements and compounds, a feature which, we trust, may prove of use, to medical students more especially. The *distinguishing tests* of every element or compound have also, as a rule, a special paragraph allotted to them.

In conclusion, we cannot refrain from expressing an earnest wish that Inorganic Chemistry may, in the future, again receive its due share of attention at the hands of Chemists; the field of research which it offers is as boundless as that afforded by Organic Chemistry, and the number of facts, relating even to the best-known and most common elements, which still require confirmation, correction, or elucidation, is far greater than would be believed by any one who has not had the special opportunity of examining them which of necessity occurs in teaching.

A. DUPRÉ.
H. WILSON HAKE.

WESTMINSTER HOSPITAL MEDICAL SCHOOL,
CAXTON STREET, S.W., *February*, 1886.

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CHAPTER I.

INTRODUCTORY.

Definition of Chemistry.—Before commencing the detailed study of any science, the intending student, not unnaturally, desires to possess some general idea of its nature and its aim; he looks for a definition of the subject, but, finding it, must of necessity fail to comprehend its full force and meaning. For, since a definition is the outcome of the ripe knowledge and complete grasp of the adept, how shall a beginner perceive in it the adequate expression of facts with which he is unfamiliar? He must at first, therefore, rest content with an imperfect understanding of a statement whose meaning will gradually develop itself as he gains a more and more intimate acquaintance with the science.

Chemistry,[*] then, the science to be considered in the following pages, is a branch of Natural Science, and treats of certain properties of matter called into action while it is undergoing changes which involve a more or less considerable and permanent alteration of its previous characteristics.

Matter.—The first question which presents itself to us in connection with this definition is the meaning of the term *Matter*, and this alone is one of the most difficult and abstruse questions which can engage our attention. But, without entering into any metaphysical speculations involving its very existence, we may define matter as *that which can be perceived by the senses.*

Reflecting on this definition of matter, we can scarcely fail to perceive the enormous variety in which it presents itself to our senses, whether *solid*, as in the multitudinous forms of the animal, vegetable, and mineral kingdoms; or *liquid*, as water; or *gaseous*, as steam or air At one time we are attracted by its shape, as in crystals; at another, its most prominent feature is some particular colour or smell, as in a flower; now its lightness, as in a cork, or its weight, as in lead, forces itself on our attention. Or, again, like wood, it may be used for

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[*] Χημεια, Egypt. Chemistry, *i.e.*, Egyptian Art.

obtaining fire, or, like water, for extinguishing it. In short, we find that every variety of matter possesses properties peculiar to itself, which distinguish it from other kinds, and constitute it a special kind of matter.

Fundamental Properties of Matter.—The study of these characteristics of matter, which we call *properties*,* constitutes *Natural Science*. None of these special characteristics can be used for the recognition of matter in general, for it is of their very essence to apply to special kinds of matter only. There are, however, certain properties common to all kinds of matter, characterising matter as such, and which, therefore, cannot be absent in any kind. These *fundamental properties*, as we may call them, may be stated briefly as follows:—

1. *Matter Possesses Weight.*—It is attracted towards the centre of the earth. That is to say, if unsupported, it falls towards the centre of the earth, and if supported, it exerts a certain pressure on its support.

On a superficial view this seems to be in contradiction to certain well-known facts. Thus, a balloon, when released from its moorings, ascends, moves away from the earth instead of falling towards it; but, as we shall see later, the supposed contradiction is apparent only and not real.

2. *Matter Occupies Space.*—That is to say, it has dimensions in three directions—length, breadth, and thickness. The amount of space so occupied may, of course, vary to an almost infinite extent, but even the smallest conceivable particle of matter still has dimensions in three directions.

3. *Matter is Impenetrable.*—That is to say, the space occupied by any given quantity of matter is occupied to the absolute exclusion of everything else.

Physical and Chemical Properties of Matter.—The second question which arises in connection with our definition of Chemistry is—Are all the changes which are going on around us chemical changes? To this we may at once answer, No. An attentive consideration of such phenomena will show us that they may be distinctly classified under two heads.

In the one class, the changes which are occurring are more or less transient and superficial; in the other class, they are more or less permanent and deep-seated. The former kind are known as *physical*

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* The term *property*, in its more scientific sense, may be defined as a characteristic of any substance, its behaviour to other kinds of matter, or the particular manner in which it affects the senses.

changes, the latter as *chemical*. Let us first select a few examples of physical changes. In winter water becomes solid, becoming liquid again on the appearance of warmer weather. All water surfaces give off vapour, and, owing to this fact, small quantities of water disappear, and things that are wet become dry on exposure to the air. This evaporation, though not so noticeable in large masses, goes on from all water surfaces without exception, the vapour thus produced descending again in the form of rain, snow, dew, &c. To take another example:—all iron structures have to be built so as to allow of a certain freedom of movement, since all such are sensibly larger in summer than in winter; the iron rails of our railways have for this reason to be laid down with small intervals between each of them. These phenomena take place without any permanent change occurring in the matter itself. Iron remains iron whether longer in summer or shorter in winter; ice or steam becomes reconverted into water with all its original properties by a mere difference of temperature. In no case has anything been added or taken away. Other examples of physical changes are the sounding of a stretched string, or of a bell when struck; the magnetisation of iron and many more will occur to all on reflection.

Let us now consider some chemical changes. Iron exposed to the action of moist air becomes converted into a brown brittle material, it rusts; animal and vegetable substances so exposed gradually disappear; the green leaves of spring and summer become brown in the autumn, fall and rot away. In all these phenomena it will be found that the changes have gone far deeper than in the former. Substances have been produced differing widely from the substances from which they were formed, and in each case something has been added or taken away. Iron rust will be found to be heavier than the iron from which it was produced; brown leaves are lighter than the green, and so on.

Just as we speak of the physical and chemical changes of any substance, so also we may speak of its *physical* and *chemical properties*. For instance, a piece of sulphur is yellow; it can be scratched by a knife, but scratches a piece of chalk—that is, it has a certain hardness; when rubbed, it becomes electric—that is, it acquires the property of attracting light bodies, which it had not before. When placed in a test-tube to which heat is applied, it becomes liquid, and may even become converted into vapour; but, on removing the source of heat, the vapour condenses again to a liquid, the liquid solidifies, and assumes the ordinary form of sulphur, with which we started. All these properties of sulphur are *physical*. During their manifestation the sulphur retains its individuality as sulphur. The changes which it has undergone are transient and superficial.

If, however, we take a piece of sulphur and heat it in contact with air on any suitable support, the sulphur will take fire, burn, and disappear, its place being occupied by a colourless gas of very pungent odour, which we must at once admit is something totally different from sulphur, and which no one would think of calling sulphur any longer. This property of sulphur—of taking fire when heated in contact with air, and being converted into a gas (by addition of or union with a part of the air)—is a chemical property, and during its manifestation the sulphur has undergone a deep-seated and permanent change.

Indestructibility of Matter.—Whatever the changes, physical or chemical, which matter may undergo, it is in no case destroyed. Matter is indestructible. This is not always easy to understand, when the change is accompanied by a total visual disappearance of matter, as in the evaporation of water, the decay of animal and vegetable substances, the burning of sulphur or of a candle; but we may well postpone further explanation of this subject at present.

Analysis and Synthesis.—We may now consider chemical changes more especially.

From what we have said it will be seen that the number of chemical changes going on around us in nature, or possible to be brought about by artificial means, must be very vast; and it would also appear that they must be very complex. That their number is vast, is true; but their complexity vanishes very soon, for we learn by experience that, notwithstanding their great number, they are of two kinds only. Either two or more substances are coalescing to form some new substance differing widely in its properties from those of its components (as in the burning of sulphur, or in the rusting of iron in air); or the reverse action is taking place, that is, some substance is splitting up into two or more substances whose properties also differ widely from those of the substance from which they are derived (as in the decay of animal and vegetable matter).

The first kind of chemical change or action is called *Synthesis;*[*] the second, *Analysis.*[†] All the multitudinous chemical changes occurring in nature or produced by artificial means belong to the one class or to the other.

Elements and Compounds.—If now we apply a system of analysis to

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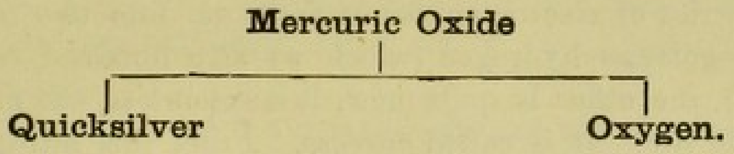
[*] *σύν, together; θέσις, a placing.*

[†] *ἀνὰ, again; λύσις, a setting free.*

natural substances, we shall find that many of them, and these among the most familiar, cannot be split up at all, and appear to consist of one kind of matter only. Such as these are iron, copper, lead, tin, silver, and gold, sulphur (or brimstone), diamond and black-lead, phosphorus, &c.

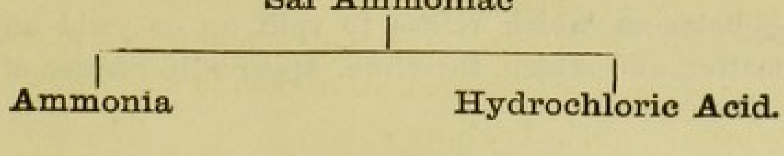
By far the vast majority of natural substances, however, can be split up into other and different kinds, but if we continue to apply the process to the products which we obtain in the first instance, we come in all cases, sooner or later, to substances which refuse to be split up, and which appear to consist of one kind of matter only. Two examples will suffice to make this clear:—*

If we take a red powder, known as mercuric oxide, and heat it strongly, it splits up into two new substances, both very different from the original substance. One is a gas called *oxygen*, the other is *quicksilver*. But both oxygen and quicksilver refuse to be further split up. The facts may be graphically represented thus·



We may now take a more complex instance. A substance known as sal ammoniac or chloride of ammonium, when treated with sulphuric acid (oil of vitriol), gives off a colourless, pungent-smelling, irritating gas, called *hydrochloric acid*, which turns blue litmus red, and which is very soluble in water.

If we treat the sal ammoniac with lime instead of oil of vitriol, we also get a colourless pungent-smelling gas, called *ammonia*, whose odour is, however, not unpleasant and very different from the one we obtained with sulphuric acid; it is also very soluble in water, but it restores the blue colour to reddened litmus. Representing this result as before, we have:—



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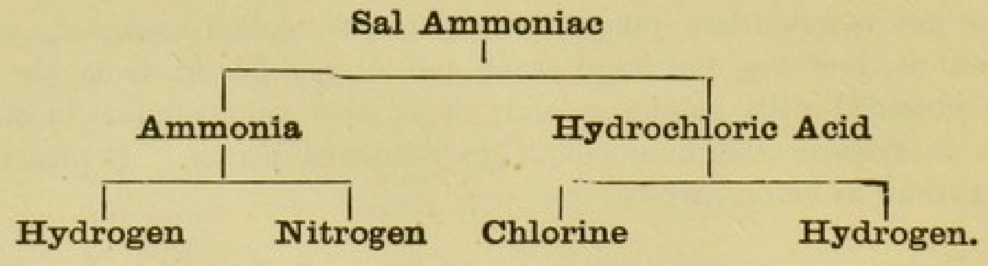
* Details of these experiments will be found in the portions of this work relating to the substances mentioned.

If these two colourless gases are brought together, dense white fumes are formed, and these white fumes finally condense to a solid, which is evidently the sal ammoniac from which they were obtained.

But these two gases obtainable from sal ammoniac may be further split up or "analysed." If we dissolve hydrochloric acid in water, and add zinc to the solution, the zinc dissolves in the acid, and a new kind of gas called *hydrogen* is given off, which is colourless, has no smell, and takes fire when a light is applied to it; but, if the hydrochloric acid solution be heated with black oxide of manganese, a green gas is obtained called *chlorine*, of peculiar odour and properties. If hydrogen and chlorine are brought together and a light applied, they explode, and form hydrochloric acid gas; but from hydrogen and chlorine we can get nothing further by analysis. They refuse to be split up.

The other kind of gas which can be obtained from sal ammoniac by means of lime, and which we call ammonia, may, like the hydrochloric acid gas, be further "analysed." If it is subjected to the action of a series of electric sparks, it splits up into two new gases—one we recognise as hydrogen (which we also obtained from hydrochloric acid), the other is quite new, it is colourless, has no smell, but will not take fire. It is called *nitrogen.* From this nitrogen we can obtain nothing further by analysis. It also refuses to be split up. Thus, sal ammoniac yields us ammonia and hydrochloric acid; ammonia yields us hydrogen and nitrogen; and hydrochloric acid yields us chlorine and hydrogen; but from chlorine, hydrogen, and nitrogen, we are unable to obtain any new substance. Representing this result as before, we have:—



Those substances, which refuse to split up or yield any different kind of matter, and which, therefore, apparently consist of one kind only, we call *elements.*

We do not wish to affirm that substances so arrived at are in every, or even in any, case truly elementary, but what is meant to be implied is that they refuse, when subjected to our present methods of analysis, to yield anything different to themselves. This is by no means a proof that they are elements. As a general rule, the more complicated a substance is, the more readily it yields to means employed to split it up. The products so obtained are naturally of simpler constitution than the substances from which they are derived, and as we continue the process of analysis we obtain simpler and simpler substances. With this greater simplicity, however, arises in each case a greater difficulty of analysis, and our present *elements* may, in reality, be substances of such comparatively simple constitution that our present means of decomposing them are insufficient. We are strengthened in this view by several examples—notably that of the hydrated oxides of the alkali metals, which at the beginning of the century were considered to be *elements*, but which in the hands of Sir Humphry Davy yielded to the then newly discovered force of electricity, and were split up into three kinds of matter, two of which were known, and all three now ranking as elements. The same remarks apply to uranium, vanadium, and some other substances, compounds of which were taken for elements, but which later on were decomposed.

Any substance consisting of more than one element we term a *compound*. By far the overwhelming majority of substances are compounds, consisting of two, three, four, and sometimes more elements. Considering the vast number of compounds known, the number of elements appears very limited in comparison with them. There are at present (A.D. 1892) only 70 known, and of these a very small number, about 16, make up the bulk of the earth's crust;* of the rest some are less abundant, some are of rare, and others of very rare occurrence.

On the following page is a complete list of the elements known up to the present time, arranged in the order of their discovery.

* These are, approximately in the order of their abundance—oxygen, hydrogen, nitrogen, silicon, chlorine, sodium, aluminium, carbon, iron, potassium, calcium, magnesium, sulphur, phosphorus, iodine, and fluorine.

THE ELEMENTS

ARRANGED IN THE ORDER OF THEIR DISCOVERY.

NAME.	DISCOVERER.	YEAR.
Carbon	Known to the Ancients	...
Copper	Known to the Ancients	...
Gold	Known to the Ancients	...
Iron	Known to the Ancients	...
Lead	Known to the Ancients	...
Mercury	Known to the Ancients	...
Silver	Known to the Ancients	...
Sulphur	Known to the Ancients	...
Tin	Known to the Ancients	...
*Antimony[1]	Basilius Valentinus	1490
Bismuth	Known to Agricola	16th century.
*Zinc[2]	Known to Agricola	...
*Fluorine[3]		17th century.
Phosphorus	Brand	1669
*Arsenic[4]	Schröder	1694
Magnesium[5]	Grew	1695
Cobalt	Brandt	1735
Platinum	Wood	1741
Nickel	Cronstedt	1751
Hydrogen	Cavendish	1766
Nitrogen	Rutherford	1772
Barium[6]	Scheele	1774
Chlorine	Scheele	1774
*Manganese	Scheele	1774
Oxygen[7]	Priestley, Scheele	1774
Molybdenum[8]	Hjelm	1782
Tellurium	Müller von Reichenstein	1782
Tungsten	J. & F. d'Elhujar	1783
Uranium[9]	Klaproth	1789

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[1] *Antimony.*—The pigment used for the eyebrows mentioned in Ezekiel xxiii. 40, and 2 Kings ix. 30, was, without doubt, antimony sulphide.

[2] *Zinc.*—Brass is mentioned by Aristotle, but the presence of zinc in it was not known till much later.

[3] *Fluorine.*—Schwanhardt in 1670 showed that *fluor-spar* mixed with a strong acid etched glass.

[4] *Arsenic.*—Arsenic compounds are mentioned by Aristotle.

[5] *Magnesium.*—An account of a peculiar salt (magnesium sulphate) found in the springs at Epsom, was first published by Nehemiah Grew, Secretary of the Royal Society, in 1695. Among numerous other investigators of magnesium compounds, Hay first showed the presence of this salt in sea-water in 1710; Davy isolated the metal in 1808.

[6] *Barium.*—Scheele first pointed out that *heavy-spar* contained a new earth. Further investigations were made by Gahn and Bergman in 1775. Fourcroy and Vauquelin prepared the oxide in 1797. The metal was isolated by Berzelius and Pontin, and by Davy in 1808.

[7] *Oxygen.*—Priestley and Scheele discovered oxygen independently. Lavoisier suggested the name *oxygen*.

[8] *Molybdenum.*—Scheele in 1778, and Bergman in 1781, were aware of the existence of the sulphide, and may be considered co-discoverers with Hjelm, who first isolated the metal.

[9] *Uranium.*—Péligot in 1841 proved Klaproth's supposed metal to be an oxide.

NAME.	DISCOVERER.	YEAR.
Zirconium[10]	Klaproth	1789
Titanium	Gregor	1789
Strontium[11]	Crawford	1790
Yttrium	Gadolin	1794
Chromium	Vauquelin	1797
Beryllium (Glucinum)	Vauquelin	1798
Vanadium[12]	del Rio	1801
Iridium	Tennant	1802
Tantalum[13]	Ekeberg	1802
Osmium	Tennant	1804
Palladium	Wollaston	1804
Rhodium	Wollaston	1804
Cerium	Klaproth, Hisinger, and Berzelius	1804
*Potassium	Davy	1807
*Sodium	Davy	1807
Boron	Davy, Gay Lussac, and Thénard	1808
*Calcium	Davy	1808
*Silicon	Berzelius	1810
Iodine	Courtois	1811
Selenium	Berzelius	1817
Cadmium[14]	Stromeyer	1817
Lithium	Arfvedson	1818
Bromine	Balard	1826
Aluminium	Wöhler	1827
Ruthenium	Osann	1828
Thorium	Berzelius	1828
Lanthanum	Mosander	1839
Didymium	Mosander	1843
Erbium	Mosander	1843
Terbium	Mosander	1843
Niobium[13]	Rose	1846
Cæsium	Bunsen and Kirchhoff	1860
Rubidium	Bunsen and Kirchhoff	1861
Thallium	Crookes	1861
Indium	Reich and Richter	1863
Gallium	Lecoq de Boisbaudran	1875
Ytterbium	Marignac	1878
Decipium	Delafontaine	1879
Norwegium	Dahll	1879
Samarium	Lecoq de Boisbaudran	1879
Scandium	Nilson	1879

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[10] *Zirconium.*—The metal was first isolated by Berzelius.

[11] *Strontium.*—Crawford first suggested the presence of a new earth in *strontianite*, basing his opinion on experiments made by Cruikshank. In 1791 Hope, and in 1793 Klaproth, came to the same conclusion, and, as it seems, independently. Davy isolated the metal in 1808.

[12] *Vanadium.*—Rediscovered by Sefström in 1830, and examined by Berzelius in 1831; but only first thoroughly investigated in 1867 by Roscoe, who first obtained the metal.

[13] *Tantalum.*—In 1801, Hatchett discovered a new metal in *columbite* from Massachusetts, which he called *columbium*. This was for many years supposed to be identical with tantalum, but was in all probability niobium, rediscovered by Rose in 1846.

[14] *Cadmium.*—Discovered independently and almost simultaneously by Hermann, Meissner, and Karsten.

* The compounds of elements marked with an asterisk were more or less known in early times.

CHAPTER II.

STRUCTURE OF MATTER.

Molecules and Atoms.—In many cases masses of matter are perceptibly made up of a number of particles of greater or less size. For example, a heap of sand is made up of particles of greater or less fineness, but still of a size readily distinguishable to the eye or to the touch. Sandstone is seen to be similarly constituted; but, whereas, in the case of the sand the particles are free to move, in the sandstone they are kept firmly together. In a piece of chalk the unaided eye does not see any particles, but a microscope will readily demonstrate that chalk is also made up of particles. If now we examine a lump of moist clay we shall find that neither the sense of touch, nor the eye, even when aided by the most powerful microscope, will enable us to recognise any particles whatever. If, however, we take the piece of clay and stir it up with water, in which the clay is perfectly insoluble, the water becomes turbid, the clay has in fact broken up and become diffused through the water in the form of exceedingly minute particles, too small to be individually recognisable, but clearly perceptible as turbidity or cloudiness. Here, then, we can neither feel nor see the particles singly, and yet we can have no doubt of their existence.

Now, let us go a step farther. Most kinds of matter appear to our senses, aided or unaided, to possess a perfectly continuous or homogeneous * structure; and yet there are so many properties of matter which admit of explanation only on the assumption that it is made up of particles, that we have no hesitation in taking for granted that this is really the case. To our mind's eye the particles are as clear as are the sand grains to our bodily eyes, or as the fact of a turbid mixture being obtained by stirring clay with water proves to us that the clay is made up of particles, although no individual particle is visible even with our most powerful microscopes.

All matter then may be supposed to be made up in the first place of individual particles (called *molecules* †), not admitting of further subdivision without destroying the character of the matter composed of these particles; and, in the second place, these particles themselves are

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* ὁμὸς, *the same;* γένος, *kind.*

† Molecula, *a small mass.*

supposed to be made up in almost every case of still smaller particles (called *atoms* *), which are to our present means indivisible. †

These molecules are of course exceedingly minute, far more minute than the smallest particles visible under our microscopes, but having nevertheless a definite size and weight.

The probable size, or, rather, the limits of size of these molecules has been calculated by Sir W. Thomson, who finds that their diameter ranges probably between 0·000000001 and 0·00000000005 of a millimetre, or something like from ten thousand to two hundred thousand times smaller than the smallest particle visible under our best microscopes. In order to convey some notion as to size, which the above figures entirely fail to do, Sir W. Thomson gives us the following illustration:—Suppose we could magnify an ordinary drop of water to the size of a globe equal to our earth, then the molecules of the water would become visible, and would be found to be larger than small shot, but smaller than cricket-balls.

Matter, then, is made up of molecules, not in actual contact, but kept at certain distances apart. We have further every reason to believe that these molecules are in unceasing motion (see ch. vi., p. 38).

Solids, Liquids, and Gases.—The special properties and conditions of any particular kind of matter depend, as we shall see more clearly later on, upon the nature of the atoms which make up the molecule, the distances at which the molecules are from one another, and the character and extent of their motion. The molecules of solids and liquids are held together by a force of attraction called *cohesion*.‡ If this force is so powerful as to keep the molecules firmly bound together, a solid substance is the result. In a solid the molecules are not free to move, but retain their relative position; the solid has a definite shape which it retains unless this

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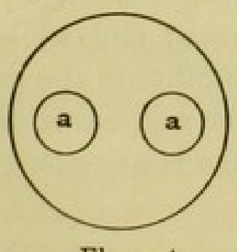
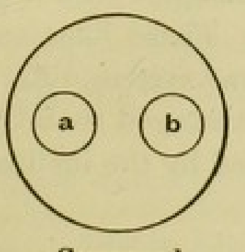
* *ἄτομος, uncut, indivisible.*

† The molecules in any given compound or element are identical *inter se*, and this identity as regards kind of matter, extends in the case of an element to the atoms, whereas, the atoms in the molecule of a compound are essentially different, being composed of different kinds of matter. The fact may be diagrammatically expressed thus:—



Element.



Compound.

‡ Cohæreo, *I stick together.*

is forcibly altered. If the cohesive force becomes less, thus allowing a greater freedom of movement to the molecules, a liquid is the result, which has no shape of its own, but adapts itself to the shape of any vessel in which it is placed, its free surface being always level. When, finally, the cohesive force becomes *nil*, a gas results. A gas always fills entirely and uniformly any vessel, great or small, in which it may be placed. The molecules of a gas, instead of attracting, have a tendency to recede from one another.

The indestructibility of matter (p. 4) presents itself in a clearer light after the above considerations. Matter may be made to undergo various changes and transformations, but in all of these the weight of the matter acted upon remains unaltered, or, to express it in language which we shall now be able to understand, the molecules of matter may be broken up or their internal structure altered, but the atoms remain unaltered throughout all changes which it may undergo.

CHAPTER III.

CRYSTALLOGRAPHY.

Most substances, when passing slowly from the gaseous or liquid condition to the solid, assume a definite geometrical form, bounded almost always by plane surfaces.* These geometrical forms are termed *crystals.* Their number and variety is considerable, but an attentive study of their characteristics has shown that they may all be ranged under a few classes, systems, or families. The members of each system have certain characteristics in common, wherein they differ from the members of all other systems.

In all systems the planes of the crystals are assumed to be disposed round certain imaginary lines passed through the crystals in a symmetrical manner. These lines are called *axes*,† and while the crystals of one and the same system differ from each other in the manner in which the planes are arranged round the axes, the crystals of different systems are distinguished by the inclination and the relative lengths of the axes.

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* κρύσταλλος, *ice.*

† Most crystals show a tendency to split in certain directions (cleavage), and the surfaces so formed are also plane.

There are in all six systems; in five of these three axes are assumed, in one of them four. The relative position of the axes is supposed to be such, that their point of intersection is the geometrical centre of the crystal, that they pass in and out of the crystals at corresponding points, and that the planes can be arranged in relation to them in the simplest and most symmetrical manner.

We may now take them in order:—

I. **Regular or Cubical System.**—Three axes, all cutting each other at right angles, and all of equal length.

II. **Square Prismatic, Quadratic, Pyramidal or Tetragonal* System.**—Three axes, all cutting each other at right angles, but one of them shorter or longer than the other two.

III. **Right Prismatic or Rhombic System.**—Three axes, all cutting each other at right angles, but all of different lengths.

IV. **Oblique Prismatic or Monoclinic† System.**—Three axes, two cutting one another at right angles, the third inclined to the plane formed by these at an angle other than 90°, and all axes of unequal lengths.

V. **Doubly Oblique, Anorthic‡ or Triclinic§ System.**—Three axes, all cutting each other at angles other than 90°, and all unequal in length.

VI. **Hexagonal‖ or Rhombohedral¶ System.****—Four axes, three in one plane cutting each other at angles of 60°; the fourth at right angles to the plane formed by the other three, the three axes in one plane being equal in length, the fourth longer or shorter.

Behaviour of Crystals to Heat and Light.—Crystals of the regular system expand equally in all directions when heated; they also conduct heat equally in all directions, and refract light singly in all directions.

Crystals of the other systems expand unequally in different directions when heated, conduct heat differently in different directions, and, except in certain directions, refract light doubly.

Size and Shape.—In the regular system simple crystals of the same genus, having all axes equal and at right angles, may differ from each other in size, but must always have the same shape; whereas, in all other systems, in which the relative lengths and inclination of the axes vary, they may not only differ in size, but also in shape or form (see figs. *g* and *h*).

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* *τέτρα, four; γόνυ, angle.*

† *μόνος, one; κλίνω, I incline.*

‡ *ἀν, not; ὀρθὸς, straight.*

§ *τρεῖς, three; κλίνω, I incline.*

‖ *ἓξ six; γόνυ, angle.*

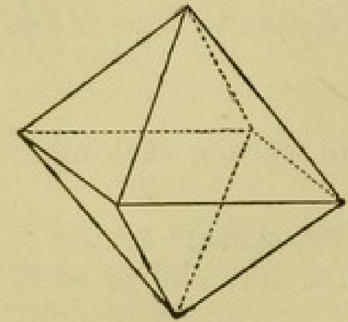
¶ *ῥόμβος, a rhombus; ἕδρα, a face.*

** We have given this system, with its *four* axes, the last place, contrary to the usual order (it is generally placed third), because we believe that such an arrangement is far more easily remembered.

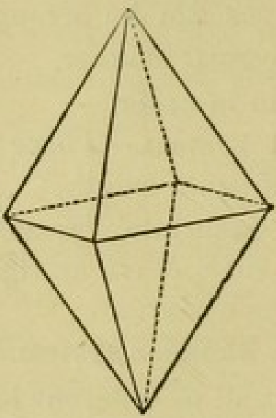
Representative Forms of the Six Systems.

A. Octahedra.

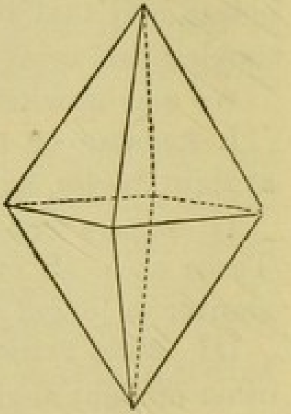
I.



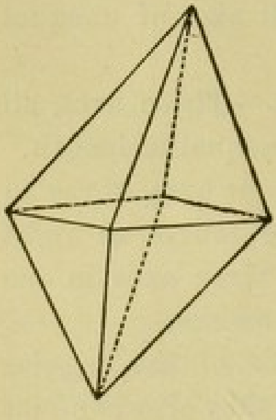
II.



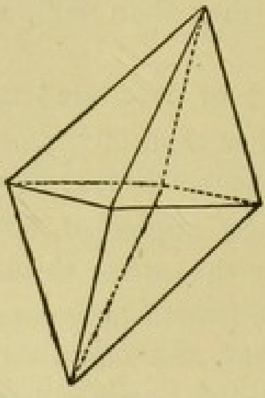
III.



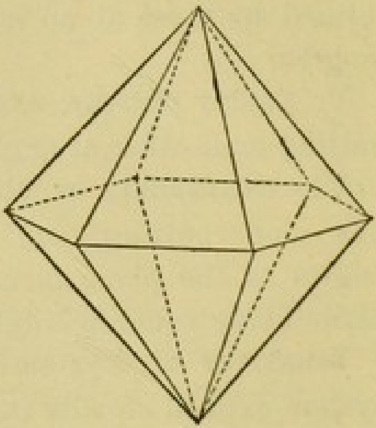
IV.



V.



VI.



Natural crystals are not always absolutely symmetrical in shape, but very frequently some of the planes are developed unduly at the expense of the others; but, however great this apparent distortion may be, the inclination of the faces towards each other remains always the same, that is, as it would be in the perfectly symmetrical crystal.

Composite Crystals.—Crystals rarely consist of a simple form, but are generally a combination of two or more forms belonging to the same system, and such are termed composite crystals.

Holohedral and Hemihedral Crystals.—Crystals in which all the faces present have the same relation to the axes, and possessing all such possible faces, are termed *holohedral** crystals. Forms derived from these by suppression of half the number of faces are termed *hemihedral*.†

The cube and the four-sided prisms have no hemihedral form; three

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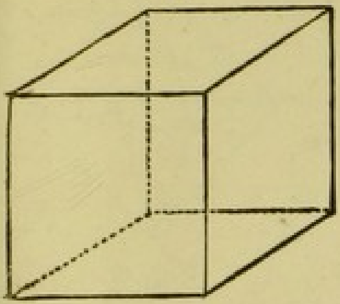
* ὅλος, *whole*; ἕδρα, *a face*.

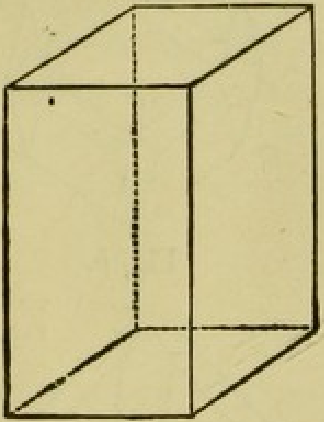
† ἡμι, *half*; ἕδρα, *face*.

B. Prisms.

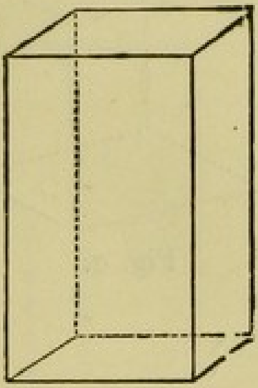
Ia.



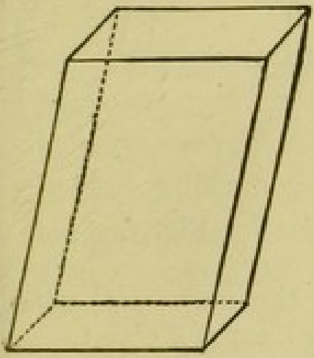
II*a*.



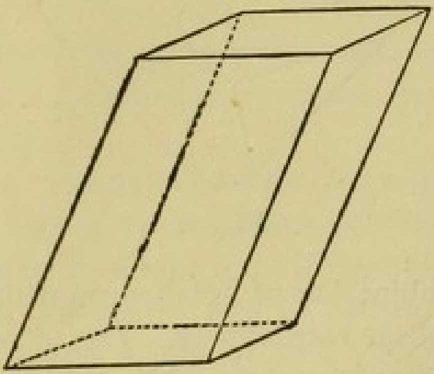
III*a*.



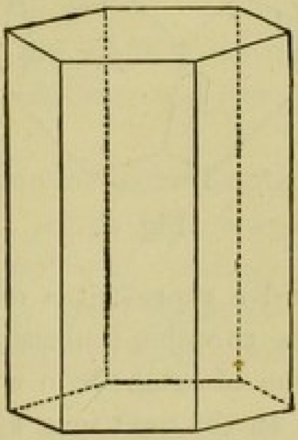
IV*a*.



V*a*.



VI*a*.



plane surfaces cannot inclose a space, but in the case of the prisms any two alternate faces may be present in a composite crystal, and are then called side or end faces, according to their position on the crystal.

Twin Crystals.—Not unfrequently two or more crystals of the same form are found grown into another in such a manner that part only of each crystal is present. Such crystals are termed twin crystals, and they always show re-entering angles or corners which are never found in other crystals.

Common Forms.—The three simplest forms in the regular system are the *cube* (fig. *a*), the rhombic *dodecahedron** (fig. *b*), and the *octahedron*† (fig. *c*). In the cube each plane cuts one axis, and is parallel to the other two. In the rhombic dodecahedron each plane cuts two axes at equal distances from the centre, and is parallel to the third. In the octahedron each plane cuts all three axes at equal distances from the centre. Figs. *d*

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* δώδεκα, *twelve*; ἕδρα, *a face*.

† ὀκτώ, *eight*.

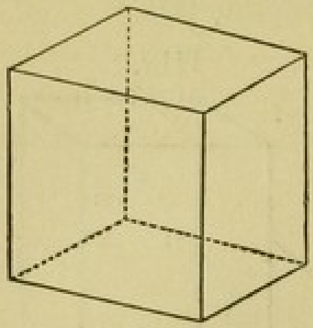
Fig. *a.*

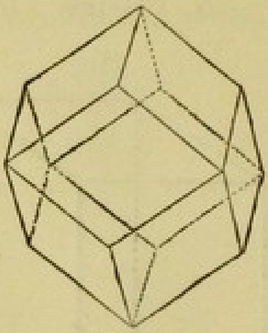
Fig. *b.*

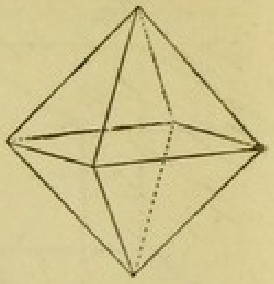
Fig. *c.*

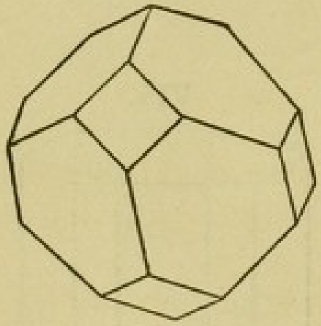
Fig. *d.*

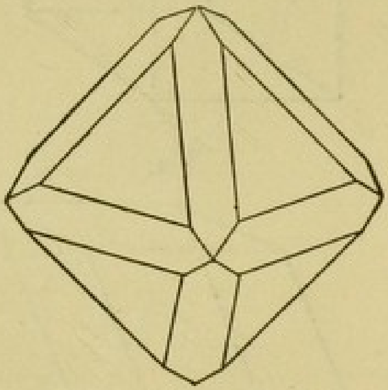
Fig. *e.*

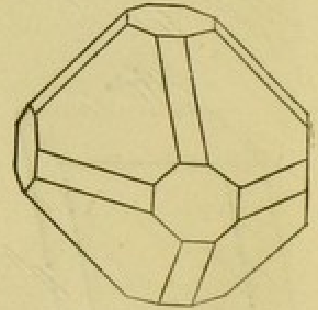
Fig. *f.*

and *e* represent a combination of octahedron with the cube, and with the rhombic dodecahedron respectively. Fig. *f* represents a combination of octahedron with cube and rhombic dodecahedron.

In the next four systems the principal forms are the *octahedron* and the *prism*, which may be taken as the representatives of the cube. These forms may vary, not only in size but also in shape, according to the varying relative lengths (figs. *g* and *h*), or lengths and inclinations

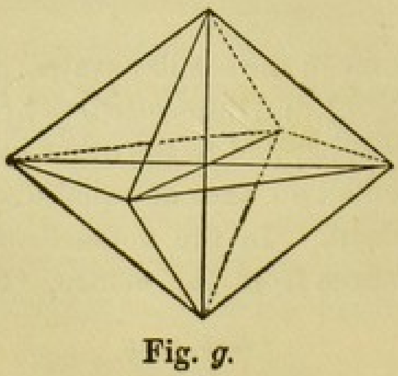
Fig. *g.*

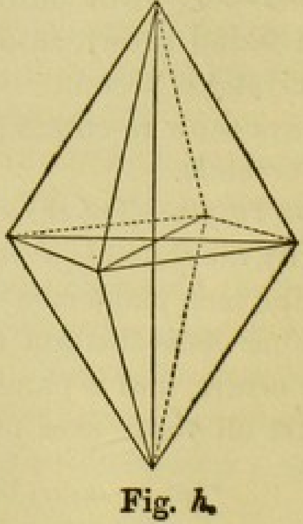
Fig. *h.*

of the axes; and, further, as to the position of the minor axes in relation to the crystals. Thus, in an octahedron or a prism, the two minor axes may terminate in the corners and angles, or in the middles of the edges or side faces. In the first case the crystals are called *direct*, in the second case *inverse* (see figs. *i* and *k*).

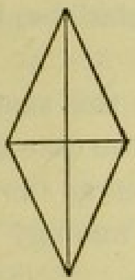

Fig. *i*.

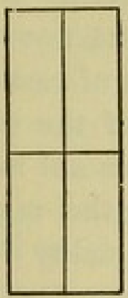

Fig. *k*.

In the sixth system the principal forms are the double six-sided *pyramid* (fig. VI), its hemihedral form the *rhombohedron*, and the *six-sided prism* (fig. VI*a*).

Dimorphism.*—Very many substances are capable of crystallising in various forms belonging to the same system. Alum and common salt, for example, may be obtained crystallised in cubes or octahedra of the regular system. Diamond also crystallises in many forms of the regular system. Calc-spar occurs in many varieties of the rhombohedral system, and so on.

A less frequently observed property is, however, the power possessed by some substances of crystallising, under varied conditions, in forms belonging to two different systems. Such substances are called *dimorphous*. This is the case, for instance, with carbon, which may crystallise in the regular system, when it constitutes diamond, or under different conditions in the rhombohedral system, when it constitutes graphite or black-lead. Again, sulphur, when crystallising from its melted condition, assumes the shape of needles belonging to the oblique prismatic system, but when crystallising from a solution of bisulphide of carbon, assumes the form of octahedra of the right prismatic system. In some few cases, substances may crystallise in three different systems and are then known as *trimorphous* substances.

Isomorphism. †—Frequently a special crystalline form constitutes a characteristic property of a substance, and indicates a certain chemical constitution. When this is the case, the process of crystallisation

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* δὶς, *twice*; μορφὴ, *form*.

† ἴσος, *equal*; μορφὴ, *form*.

becomes a most important means of obtaining the substance in a state of purity. In many cases, however, it is found that substances of different but analogous chemical composition, crystallise in the same form. This phenomenon is termed *isomorphism*, the substances being called *isomorphous*. Isomorphism may, in some cases, be a most valuable indicator of a similarity of constitution in different substances, and, hence, often enables us not only to fix the chemical relations, but even the atomic weights of certain elements (p. 62).

As crystals of the regular system, belonging to the same genus may differ in size but not in form, equality of form in the case of substances crystallising in the regular system cannot be taken as showing isomorphism, *i.e.*, equality of form accompanied by analogy in chemical constitution.

Methods of Crystallisation.—Crystals may be obtained in a variety of ways. In almost all cases crystals are the larger and more perfectly formed, the more slowly they have been produced, the greater the mass from which they are produced, or, as in case 3 (*b*), the more constant the temperature during their formation. The following are the methods in general use:—

1. *By Sublimation.*—Some solids, when heated, go off into vapour without becoming liquid, and if the vapour is cooled, it condenses crystalline. Such are iodine, arsenious acid, mercuric chloride.

2. *By Fusion*—Some solids, when melted by the application of heat, solidify in crystalline masses on being cooled more or less slowly, *e.g.*, sulphur and many metals.

3. *By Solution.*—(*a.*) If a solid substance is dissolved to saturation at an elevated temperature in a solvent in which it is more soluble in the hot than in the cold, the excess of substance dissolved at the higher temperature frequently separates out in crystals when the solution is cooled, the solvent not being able to retain it at the lower temperature. Most salts, and very many organic substances, behave in this manner, and this method of obtaining crystals is the one most frequently employed. (*b.*) If from a saturated solution of a solid, the solvent is gradually removed by evaporation (through application of heat or spontaneously), the solid is generally deposited in the crystalline form, in proportion to the removal of the solvent—*e.g.*, common salt, &c., &c.

4. *By Electrolysis.*—Many metals are deposited at the negative pole of a powerful battery in a crystalline form.

Allotropy.[*]—In some cases dimorphous (p. 17) elements show

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[*] ἄλλος, *other;* τρόπος, *form.*

strikingly different characteristics, according to the crystalline form which they assume. Thus, carbon, when crystallised in the regular system, constitutes diamond, while, when it crystallises in the hexagonal system, it constitutes graphite or black-lead. In other cases, as for example, in the case of prismatic and octahedral sulphur, the difference is more or less confined to the crystalline form.

Again, some elements exist, both in the crystalline and in the amorphous or vitreous form, and in such cases the differences of properties are often strongly marked. These remarkable differences of condition assumed by certain elements, are known as allotropic modifications. They are usually accompanied by a difference in density. This phenomenon of allotropy is not confined to solid elements, but is also found, in one striking instance at least, among gaseous elements. Oxygen, as will be shown later on, is known in a comparatively inactive, and also in a highly active condition; and this case is of especial interest, as it serves to throw a light on the probable cause of allotropy. It can be shown that, whereas ordinary oxygen contains only two atoms in its molecule, ozone or active oxygen contains three. Allotropy in other elements is probably due to a like cause.

Variations similar to the above-mentioned allotropic modifications occur also among compounds, as, for instance, in the red and yellow varieties of mercuric iodide, and in the red and black varieties of mercuric sulphide.

In crystals belonging to the quadratic and hexagonal systems there is but one direction in which they refract light singly (uniaxial crystals); and this optical axis coincides with the principal crystallographic axis. In crystals belonging to the rhombic, oblique, and doubly oblique systems, there are two directions in which light is singly refracted (biaxial crystals).

CHAPTER IV.

WEIGHTS AND MEASURES.

To measure is to ascertain how many times a quantity which is taken as a unit or standard of comparison (a unit of measure) is contained in another quantity of which it is desired to represent the amount. Thus, to measure the distance between two cities is to ascertain how many times the unit of length is contained in the distance to be expressed. To express the weight of any substance, we determine how many times a certain unit of weight is contained in it, &c., &c.

The Metric[*] System.—The metric system is a decimal system of weights and measures, devised by a Committee of the Institute of France at the request of the Government, and introduced into France at the commencement of this century. Its convenience and simplicity have caused its universal adoption in science throughout Europe.

The basis of the whole system is the *metre*[†] or unit of length, the English equivalent of which is 39·37 inches. From this unit all other units are derived, as will be seen from the following tabular statement:—

MEASURES OF LENGTH (*Multiplier* 10).

Metre = 39·370432 inches.
Decimetre = $\frac{1}{10}$ Metre = 3·937 ,, = 4 inches nearly.
Centimetre = $\frac{1}{100}$ Metre = ·3937 inch = $\frac{4}{10}$ inch nearly.
Millimetre = $\frac{1}{1000}$ Metre = ·03937 ,, = $\frac{4}{100}$ = $\frac{1}{25}$ inch nearly.

MEASURES OF SURFACE (*Multiplier* 100).

Square metre = 100 square decimetres.
= 10,000 square centimetres.
= 1,000,000 square millimetres.

MEASURES OF CAPACITY (*Multiplier* 1000).

Cubic decimetre or **Litre** = 1,000 cubic centimetres.
= 61·024 cubic inches = 1·76 imperial pint.
Cubic centimetre = $\frac{1}{1000}$ litre.

MEASURES OF WEIGHT (*Multiplier* 10).

Kilogramme = 1,000 grammes = 15,432 grs. = 2·20 lbs. av.
Gramme[‡] = $\frac{1}{1000}$ kilogramme = 15·432 grs.

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[*] *μέτρον, a measure.*

[†] The governing feature in the introduction of the metric system was, firstly, the establishment of a natural standard which could at any time be recovered, even assuming all existing copies of the standard to have been lost. This condition the metre was devised to fulfil, having been made equal to the 10,000,000th part of a quadrant of the earth, measured from the equator to the pole. Unfortunately, an error occurred in the measurement. The metre is not exactly the 10,000,000th part of a quadrant, and is now, like all other measures, based solely on the standard kept at Paris. The second feature aimed at was the intimate relation of the various measures of length, surface, and capacity; and this it fulfils in the most admirable manner, and it is chiefly this that constitutes its great value.

[‡] A gramme is the weight of 1 cubic centimetre of distilled water at 4°C.

Decigramme = $\frac{1}{10}$ gramme.
Centigramme = $\frac{1}{100}$ gramme.
Milligramme = $\frac{1}{1000}$ gramme = $\frac{1}{65}$ grain nearly.
1 cubic metre of water weighs 0·9842 ton = 1 ton nearly.

A **crith** * is the weight of 1 litre of hydrogen at 0° and 760 mm. Bar. = 0·0896 gramme.

The following **English weights and measures** are often required:—

AVOIRDUPOIS WEIGHT.

1 lb. = 16 ozs. = 7,000 grains.
1 oz. = 437·5 grains.

APOTHECARIES WEIGHT.

1 lb. = 12 ozs. = 5,760 grains.
1 oz. = 480 grains.

1 gallon weighs 10 lbs. av., or 70,000 grains.
1 pint contains 20 fluid ozs.
1 cubic foot of water weighs 997 ozs. = 1,000 ozs. av. nearly.

CHAPTER V.

SPECIFIC GRAVITY.

Specific Weight of different Substances.—Weight, as already stated (p. 2) is a fundamental property of matter. If we compare different bulks of the same kind of matter as regards their weight, it is self-evident that their relative weights vary as their respective bulks. Thus, ten cubic inches of iron weigh ten times as much as one cubic inch of iron.

This simple and obvious relation between bulk and weight, however, ceases to hold good as soon as we compare different kinds of matter. In this latter case, the least consideration will remind us that often very bulky things possess but little weight, and that very heavy things often occupy but a small bulk; that, although weight is a fundamental property of matter, all kinds of matter are not equally

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* *κριθή, a barley corn.*

heavy, bulk for bulk; they possess, in fact, a specific weight, gravity or density.[*]

This specific weight of different kinds of matter often constitutes an important distinguishing property, and, for the sake of uniformity and convenience, the weights of all solids and liquids have been compared with the weight of an equal bulk of water taken as unity. The resulting number tells us how many times heavier or how many times lighter the substance is than water, bulk for bulk, and is most commonly called the **Specific Gravity** of the substance.

In order to insure absolute uniformity in the statement of results, it has been generally agreed upon to take one special substance, viz., water for comparison with all the rest, and to express the specific gravity of all solids and liquids in relation to such a chosen standard; now, inasmuch as all substances alter in bulk, and, consequently, in the relative weight of equal bulks by change of temperature, it is not sufficient to fix upon one special standard, but it is also necessary to fix upon a particular temperature at which the comparison is made. Unfortunately we find here no longer a universal agreement. In England the temperature chosen is 15·5°C. (60°F.); on the Continent it is 4°C.[†] Now, on heating water from 4°C. to 15·5°C it increases sensibly in bulk, but of course does not alter in weight. Thus, 10,000 volumes becomes 10009·5 at 15·5°C., and, therefore, 10,000 volumes measured at 15·5° will weigh less in the same proportion compared to 10,000 volumes at 4°. Or, taking the specific gravity of water at 4° as 1, its specific gravity at 15·5 will be 0·999050; and, conversely, taking the specific gravity at 15·5° as 1, its specific gravity at 4° will be 1·00095. The standard taken for comparison on the Continent is, therefore, slightly higher than in England, in consequence of which the specific gravities of substances, as given in Continental books, are slightly lower than those given for the same substances in English books.

Determination of the Specific Gravity of Solids and Liquids.—To determine the specific gravity of any solid or liquid two data only are necessary, viz.:—

1. The absolute weight (a) of any given bulk of the substance;
2. The weight (b) of an equal bulk of water;

$$\text{then } \frac{a}{b} = \text{the specific gravity of the substance.}$$

To arrive at these data various methods have been devised. We may consider the case of liquids first as presenting the least difficulty.

A. LIQUIDS.

(1.) **By Weighing Equal Volumes of the Liquid and Water.**—This may be effected by weighing the liquid and water successively in the same vessel, care being taken that the vessel is completely filled each time.

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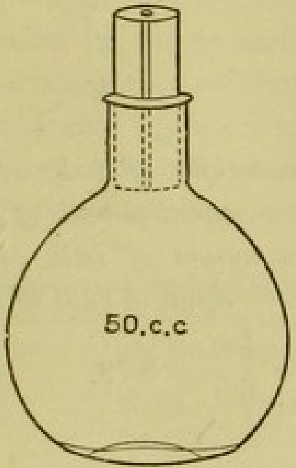
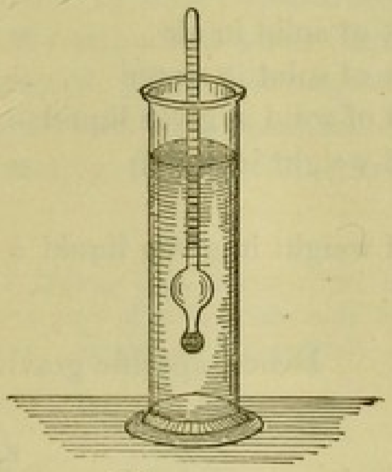
[*] Strictly speaking, density means comparative *mass*, while specific gravity or specific weight denotes comparative *weight;* but, as mass and weight are proportional to one another, the two terms may be (and in chemical text-books frequently are) used indifferently.

[†] This temperature has been selected as corresponding to the *maximum density* of water (*q.v.*)

The accuracy of the result depends chiefly on the degree of accuracy with which the vessel can be filled, so as always to contain the same volume. A variety of vessels, known as specific gravity flasks, has been devised with a view to attaining such accuracy, most of which have a capillary tube in the stopper, or at the side, so that the stopper can be inserted without danger of retaining a bubble of air, the excess of liquid escaping through the capillary tube. The temperature of both the liquid and the water must be carefully observed, and an allowance made for deviation from the standard temperature, or both must be brought to the standard temperature before weighing.



Specific Gravity Flask.



Hydrometer.

*Example:**

Weight of specific gravity flask + liquid at 15·5°C. = 81·6 grms.
Weight of specific gravity flask + water at 15·5°C. = 72·3 ,,
Weight of specific gravity flask = 22·3 ,,

$$\text{Hence, specific gravity of liquid} = \frac{81{\cdot}6 - 22{\cdot}3}{72{\cdot}3 - 22{\cdot}3} = \frac{59{\cdot}3}{50} = 1{\cdot}186.$$

(2.) **By Hydrometers**† **or Areometers.**‡—A hydrometer or areometer is an instrument by means of which it is possible to read off, or to rapidly calculate, according to some scale of degrees, the specific gravity of the liquid in which it is placed. Its construction is based on the principle

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* Strictly speaking, the so-called *empty* bottle is full of air, and the weight of the empty bottle is really the weight of the bottle *plus* the weight of air it contains. When the bottle is filled with liquid this air is expelled, and is not included in the weight of the full bottle. The weight of the liquid filling the bottle is therefore really too low. In accurate experiments allowance for the weight of this air has to be made, and if the experiment is made at other than the standard temperature, allowance must be made for the expansion of the glass of the bottle, as well as for that of the liquid.

† Hydrometer, *ὕδωρ*, *water*; and *μέτρον*, *a measure.*

‡ Areometer, *ἀραιός*, *thin*, *rare*; and *μέτρον*, *a measure.*

that a floating body displaces a bulk of the liquid in which it floats, such that the weight of the bulk of liquid displaced is equal to the whole weight of the floating body. In shape it somewhat resembles a fishing-float. It is made of glass or metal, and is so weighted as to float upright. A narrow stem permits it to indicate small variations in the specific gravity of the liquids tested.

(3.) **By Weighing a Solid in the Liquid and in Water.**—This method is based on the principle that a body, when weighed in a liquid of less specific gravity than itself, appears to weigh less than its weight in air, by the weight of an equal bulk of the liquid in which it is immersed.

The following example will best illustrate the method:

Weight of solid in air = 25·4 grms.
Weight of solid in water = 18·9 ,,
Weight of solid in given liquid = 20·6 ,,
Loss of weight in water = 6·5 ,, = *weight of bulk of water equal to bulk of solid.*
Loss of weight in given liquid = 4·8 ,, = *weight of bulk of liquid equal to bulk of solid.*

Hence, specific gravity of liquid $= \frac{4·8}{6·5} = 0·73.$

B. SOLIDS.

(1.) **By Weighing the Solid in Air and in Water.**—This method depends on the principle already mentioned (A. 3), that a body of greater specific gravity than a given liquid, will, when weighed in the liquid, weigh less than its whole weight by the weight of an equal bulk of the liquid. Hence, the loss of weight of the solid in water, represents the weight of an equal volume of water, and we have only to divide the weight in air by the loss of weight in water to find the specific gravity.

Example:

Weight of solid in air = 36·5 grms.
Weight of solid in water = 28·7 ,,
Loss of weight in water = 7·8 ,, = *weight of bulk of water equal to bulk of solid.*

Specific Gravity of solid $= \frac{36·5}{7·8} = 4·679.$

(2.) **By Weighing a Solid in Air and in a Bottle previously Weighed and full of Water.**—By this method the difference in weight gives the weight of the water displaced, *i.e.*, of an equal volume of water. An example will best explain it.

Example:

Weight of bottle full of water (75·6) + solid (19·2) *outside* = 94·8 grms.
Weight of bottle full of water + solid *inside* = 92·9 ,,
Difference = weight of water displaced by solid = 1·9 ,,

$$\text{Hence, specific gravity of solid} = \frac{19\cdot2}{1\cdot9} = 10\cdot1.$$

(3.) **By Calculation from Cubical Contents.**—If the cubical contents of a solid are known and the weight of the solid, it is easy to determine its specific gravity by dividing its weight by the weight of an equal volume of water. The volume may be found by direct measurement or by immersion in water, and measuring the amount of water displaced, or by measuring the volume of air displaced, which last may be done with considerable accuracy in a specially-devised instrument called the *volumenometer*, especially suited for estimating the specific gravity of powders or porous substances.

(4.) **Determination of Specific Gravity of a Solid Lighter than Water.**—This may be effected by attaching the solid lighter than water to a piece of metal sufficiently heavy to sink it, and whose weight in air and in water is known. An example will suffice:—

Weight of piece of cork in air = 7·5
Weight of piece of metal in air = 30·2
Weight of piece of metal in water = 25·9
Loss of weight of metal in water = 4·3

Metal + cork in air = 37·7
Metal + cork in water = 3·4
Loss of weight of metal + cork in water = 34·3
Loss of weight due to metal only = 4·3
Loss of weight due to cork = 30·0

$$\text{Hence, specific gravity of cork} = \frac{7\cdot5}{30} = 0\cdot25.$$

(5.) **Determination of Specific Gravity of Solid Soluble in Water,** but insoluble in another liquid, say turpentine (specific gravity of turpentine = 0·872).

Weight of solid in air = 1·76
Weight of solid in turpentine = 1·06
Loss of weight in turpentine = 0·70

$$\text{Weight of equal volume of water} = \frac{0\cdot70}{0\cdot872} = 0\cdot802$$

$$\therefore \text{Specific gravity of solid} = \frac{1\cdot76}{0\cdot802} = 2\cdot194.$$

Determination of Specific Gravity of Gases.*—The specific gravity of gases is usually compared with air or hydrogen as the standard or unit. In estimating the specific gravity of solids or liquids, unless great accuracy is required, the temperature may often be neglected, since the differences of volume, due to changes of temperature within the ordinary range, are not such as to materially affect the result. In gases, however, owing to their greater expansive power, it is not only necessary to take the temperature into account, but also the atmospheric pressure at which all observations are made. Owing to their greater bulk, corrections have likewise to be made, both for displacement of air, and for the expansion of the vessel in which they are contained (p. 27), which is usually a glass balloon. Since also the temperature and pressure vary in different and even during the same determinations, it is necessary, in all cases, to reduce by calculation the observed volume of the gas to its *normal volume* (p. 51), that is, to the volume it would occupy at 0° and 760 mm. bar. This normal volume is often a theoretical quantity, since, as a matter of fact, many vapours cannot exist as such at 0° but would become liquid or even solid at that temperature.

This normal volume is further only true on the assumption that the gases or vapours in question, expand equally for equal increments of heat, and that they obey Boyle's law (p. 50). On the same assumption the specific gravities of any two gases must preserve the same ratio to each other as long as the temperature and pressure, whatever they may be, remain the same for both.

CHAPTER VI.

PHYSICAL BEHAVIOUR OF SUBSTANCES TO HEAT.

AMONG the characteristic properties which distinguish elements or compounds from one another, we must include their physical behaviour to heat.

Conduction.—By conduction is meant the transmission of heat through

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* This paragraph, inserted here for convenience of reference, cannot be properly understood without a previous knowledge of the effects of heat and pressure on the volume of gases, and will be best omitted by the beginner until after the perusal of ch. vi.

a body, without any simultaneous transportation of its particles. The *conductivity*, or transmitting power for heat, varies considerably for different substances. We distinguish roughly between *good conductors* and *bad conductors* of heat. The metals, as a class, are distinguished by their greater conductivity. The non-metals (p. 78), on the other hand, are on the whole bad conductors, as are also, generally speaking, liquids and gases.

Relative Conductivity of some Metals.

Silver, ...	1000	Iron, ...	119
Copper, ...	736	Lead, ...	85
Zinc, ...	190	Platinum, . . .	84
Tin, ...	145	Bismuth, . . .	18

Convection.—If a liquid or a gas be heated from *below*, so that the heated portions, which become specifically lighter, rise and give place to cooler portions from above, a circulation is thus established in the liquid, and a rapid distribution of heat ensues. This is called the process of convection.* It is in this manner that large masses of a liquid or a gas may be heated in a comparatively short time, despite their bad conductivity.

Expansion.—Most bodies, when heated, *expand*, that is, increase in bulk; and, generally speaking, gases expand far more than liquids, and liquids far more than solids, for equal increments of temperature. But, whereas, for equal increments of temperature, the relative expansion of solids and liquids varies very considerably, it is found that all gases and vapours expand at sensibly equal rates (see below).

Expansion of Solids.—In solids we distinguish between the linear, superficial, and cubical expansion. The fraction of its length, surface, or volume which a solid expands for 1°C. is termed respectively its linear, superficial, and cubical *coefficient of expansion*.

For all practical purposes the superficial coefficient of expansion is *twice*, and the cubical coefficient *three times*, that of the linear.†

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* Convectio, *a carrying together*.

† If the side of a cube of metal at 0° be unity, and a its linear coefficient of expansion, then at 1° its side will measure $1 + a$, its surface $(1 + a)^2$ and its volume $(1 + a)^3$.

Now $(1 + a)^2 = 1 + 2a + a_2$, and $(1 + a)_3 = 1 + 3a + 3a^2 + a^3$.

And since a is a very small quantity, a^2 and a^3 may be neglected.

The following figures will suffice in illustration of the above :—

Coefficients of Expansion of some Solids.

SUBSTANCE.	*Linear.*		*Cubical.*
	Between 0° and 100°	Between 0° and 300°	Between 0° and 100°
Lead, . .	$0{\cdot}0000284 = \frac{1}{35100}$	0·0000296	0·0000839
Copper, .	$0{\cdot}0000172 = \frac{1}{58100}$	0·0000190	0·0000550
Iron, . .	$0{\cdot}0000118 = \frac{1}{84700}$	0·0000134	0·0000355
Platinum, .	$0{\cdot}0000088 = \frac{1}{11300}$	0·0000089	0·0000265
Glass, .	$0{\cdot}0000086 = \frac{1}{11600}$	0·0000101	0·0000254

The rate of expansion of solids, which is practically uniform at lower temperatures, does not proceed regularly but increases at higher temperatures. Hence, their coefficients of expansion are greater at higher temperatures.

Expansion of Liquids.—In the case of liquids (except under certain special conditions), the observed rate of expansion (*apparent expansion*) is simply the difference between its actual expansion (*real expansion*) and the expansion of the material of the vessel in which it is contained.

The coefficient of expansion of liquids varies so considerably, even at lower temperatures, that it cannot be accurately expressed by a single fraction,* but only by a formula sometimes even requiring separate formulæ for various temperature intervals. Thus, if the volume of the liquid at 0° be taken as unity, and V = its volume at t°, then for mercury—

$V = 1 + 0{\cdot}000179007t + 0{\cdot}0000000252316t^2$.

For alcohol (from 0° to 79·8°),

$V = 1 + 0{\cdot}00104139t + 0{\cdot}0000007836t^2 + 0{\cdot}000000017618t^3$.

For ether (specific gravity 0·73658, boiling point 34·9°), from 0° to 33°,

$V = 1 + 0{\cdot}00148026t + 0{\cdot}0000035031 6t^2 + 0{\cdot}000000027007t^3$.

While water requires several formulæ between 0° and 100°.

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* Expressed as a rough average, the coefficient of expansion of mercury would be 0·00018, or $\frac{1}{5555}$; of alcohol 0·0011, or $\frac{1}{909}$; of ether 0·0015, or $\frac{1}{666}$.

Expansion of Gases.[*]—As already stated, all gases and vapours expand sensibly alike for equal increments of temperature, viz.: $\frac{1}{273}$ or 0·003665 of their volume at 0° for every degree Centigrade.[†] The following formula enables us, therefore, to calculate the volume of a gas at any required temperature, if we know its volume at any observed temperature:—

$$V_{t'} = \frac{V_t \times (273 + t')}{273 + t}$$

where V_t = vol. at observed temperature $t°$,
and $V_{t'}$ = vol. at required temperature $t'°$.

Temperature and Quantity of Heat.—By the *temperature* of a body we mean its *sensible heat*, and it is of great importance to distinguish clearly between temperature or *intensity of heat* and *quantity of heat.* Two substances are of the same temperature, if, when brought into contact, neither parts with any heat to the other, yet these two substances may contain very different quantities of heat.

This may be demonstrated by the following experiment:—Two balls of copper and lead respectively, and of equal weight, are placed in a water bath heated to boiling (100°), and then deposited at the same moment upon a cake of wax about a quarter of an inch thick. The copper ball will quickly melt through the wax, while the lead ball will make but little impression upon its surface. These two substances have absorbed very different *quantities* of heat, while attaining the same temperature or *intensity* of heat.

Measurement of Temperature—Thermometers.—Temperature is usually measured by the expansion or contraction of mercury in a specially constructed vessel. The *Thermometer*,[‡] as this instrument is called, generally consists of a hermetically sealed long glass tube, of regular capillary bore which terminates at one end in a bulb, completely filled with mercury, at or near the boiling point of the latter, to the exclusion of all air.

To effect its graduation it is plunged into *melting* ice, and the position of the mercury column marked off on the stem. It is next immersed in a steam bath,[§] and the position of the mercury column again

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[*] See also ch. viii., p. 51.

[†] Regnault and Magnus found that the more easily condensible gases expand rather more rapidly, thus:—

	Coefficient of Expansion (Regnault).
Carbonic Anhydride, ...	0·003709
Nitrous Oxide, ...	0·003719
Cyanogen Gas, ...	0·003876
Sulphurous Acid, ...	0·003902

[‡] *θέρμη, heat; μέτρον, a measure.*

[§] That is of steam produced from water boiling under a pressure of 760 mm. bar., or corrected for that purpose.

marked. These two *fixed points*, respectively known as the *freezing point* and the *boiling point*, give us a standard interval which serves as a basis for a scale of degrees.

For measuring moderate or very low temperatures an *alcohol thermometer* is used. It must be graduated by comparison with a mercury thermometer.

As the rate of expansion of mercury increases with the temperature, the indications of the mercury thermometer are not absolutely correct at higher temperatures; hence, where complete accuracy is required (and also for high temperatures), an *air thermometer* must be used, and this may be provided with a platinum bulb. The indications of this instrument are perfectly accurate, but involve with each observation a somewhat complicated calculation, depending upon the fact that, as the change of volume of any given bulk of air, for any known change of temperature (and pressure) can be calculated, it follows that the temperature can be calculated, if the change of volume is known (p. 51).

The following are the ranges of temperature, for which these different kinds of thermometers are available:—Mercury thermometer, from $-38°$ to 360°; alcohol thermometer, from $-100°$ to 40°; while an air thermometer is practicably available for any known temperature.

Very high temperatures may be estimated by immersing in the substance whose temperature has to be determined, a known weight of a substance, which does not melt at that temperature (generally platinum), and cooling it in a known weight of water. The rise of temperature being observed, and the specific heat of platinum known, the required temperature may be calculated (p. 31).

Or the variation of the conducting power of platinum for electricity, which diminishes as the temperature rises, may be employed.

Conversion of Degrees of Different Scales.—There are three scales in common use—that of Fahrenheit, used in England, that of Celsius (Centigrade), used in France, and that of Reaumur, used in Germany These are marked as to their freezing points respectively, 32°,[*] 0°, and 0°; and, as to their boiling points, 212°, 100°, and 80°. Hence, the standard interval in the Fahrenheit is divided into 180°, in the Celsius into 100°, and in the Reaumur into 80°; hence, the relation between their degrees is as 9 : 5 : 4.

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[*] 32° *Fahrenheit.*—A mixture of ice and salt (frequently used as a freezing mixture) attains a temperature of 32° Fahrenheit below the freezing point of water, and Fahrenheit believed this to be the lowest possible temperate, hence he took it for his *zero*. We now know that the real zero is far lower (see *Absolute Zero*, p. 39).

Owing to the common use of all these instruments, it becomes a necessity to be able to convert degrees of the one into degrees of the other. The following rules will suffice:—

To convert Fahrenheit into Centigrade and Reaumur degrees, and vice versa.—Since the Fahrenheit freezing point starts at 32°, it is necessary in converting Fahrenheit into Centigrade or Reaumur degrees, to *first subtract* 32, and in the reverse operation to *finally add* 32.

If x = degrees required, then—

$$x^\circ\ (\text{Centigrade}) = (\text{F} - 32)\frac{5}{9};\quad x^\circ\ (\text{Reaumur}) = (\text{F} - 32)\frac{4}{9}$$

$$x^\circ\ (\text{Fahrenheit})^{*} = \frac{9}{5}\,\text{C.} + 32;\quad x^\circ\ (\text{Fahrenheit}) = \frac{9}{4}\,\text{R.} + 32.$$

To convert Centigrade into Reaumur degrees, and vice versâ.—Let x = degrees required.

$$\text{Then } x^\circ\ (\text{Centigrade}) = \frac{4}{5}\,\text{R.} = 0{\cdot}8\ \text{R.}$$

$$\text{and } x^\circ\ (\text{Reaumur}) = \frac{5}{4}\,\text{C.} = 1{\cdot}25\ \text{C.}$$

Measurement of Quantity of Heat—Calorimeters.—The instruments used to determine *quantity* of heat are termed calorimeters.[†] They are used in specific heat determinations (p. 32), or in estimating the amount of heat evolved in chemical combination (ch. xii.). There are two principal kinds—(1) the water-calorimeter (2) the ice-calorimeter.

In the *water-calorimeter* the rise in temperature produced in a known weight of water, by the cooling, combination, &c., of a substance, is estimated, all loss of heat being reduced to a minimum, and unavoidable loss allowed for.

If we call the **unit of heat** the heat required to raise 1 gramme of water 1°C. (strictly speaking from 0° to 1° C.,) and the specific heat of water 1, then if m = weight in grammes of the water contained in the calorimeter (*plus* the *water-value*[‡] of the calorimeter, thermometer, and

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[*] A rapid method, not commonly known, for converting Centigrade degrees into Fahrenheit degrees, is as follows:—*Double the Centigrade degrees, and subtract from them one-tenth of their quantity, to the remainder add* 32, and the result is the corresponding number of degrees Fahrenheit. *Example*—Convert 36·2°C. into F°.

Answer. 72·4 — 7·24 + 32 = 97·16 . ·. 36·20°C. = 97·16° F.

[†] Calor, *heat; μέτρον, a measure.*

[‡] The *water-value* of the calorimeter, &c., is that quantity of water whose weight is equal to the weight of the calorimeter, thermometer (as far as immersed), and stirrer, multiplied by their respective specific heats (see *Specific Heat*, p. 32).

stirrer), and t its rise in temperature, it follows that $m\,t$ = number of units of heat given up by the substance in cooling, combining, &c.

In the *ice-calorimeter* the amount of ice melted is estimated, and since, in order to melt 1 gramme of ice, 79 units of heat are required, then if x = number of grammes of ice melted, 79 x = number of units of heat given out by the substance in the calorimeter.

Specific Heat.—By specific heat is meant the quantity of heat required to raise a given weight of any substance, through a certain range of temperature, as compared with the quantity required to raise the same weight of water through the same range of temperature. Thus, to raise a kilogram of mercury 1° requires about $\frac{1}{30}$ of the quantity of heat required to raise a kilogram of water 1°; hence, we call the specific heat of mercury 0·033.

The specific heat of a substance varies according to its physical state, being generally greatest in the liquid state, and increases at higher temperatures, as will be seen from the following few examples :—

Specific Heats of some Substances under varying Conditions.

Substance.	Solid.	Liquid.	Gaseous.	Substance.	0°–100°	0°–300°
Water, .	0·5040	1·0000	0·4805	Iron, . .	0·1098	0·1218
Bromine, .	0·0843	0·1051	0·0555	Copper, .	0·0949	0·1013
Tin, . .	0·0562	0·0637	...	Zinc, . .	0·0927	0·1015
Lead, . .	0·0314	0·0402	...	Silver, . .	0·0559	0·0611
Mercury, .	0·0319	0·0333	...	Platinum, .	0·0335	0·0355

Dulong and Petit's Law.—According to this law the quantity of heat required to raise atomic proportions (p. 57) of all solid elements through the same range of temperature is the same. In other words, the specific heat of any solid element varies inversely as its atomic weight. This law is in no case found to be absolutely correct, but is mostly approximately so only; the observed variations are probably due to variations in specific heat for various ranges of temperature, difference of physical condition, &c.

The product of the atomic weight and the specific heat of an element is called its *atomic heat*, and as will be seen from the following examples, is a constant which averages about 6·3. If, therefore, we divide 6·3 by the specific heat of a solid element, we obtain an approximation of its atomic weight which is sufficient to decide this point in doubtful cases.

Atomic Heat of some Solid Elements.

ELEMENT.	a. Atomic Weight.	b. Specific Heat.	c. Atomic Heat $= a \times b$.
Aluminium, ...	27·4	0·2143	5·87
Antimony, ...	122·0	0·0508	6·19
Copper, ...	63·5	0·0951	6·03
Iron, ...	56·0	0·1138	6·37
Lead, ...	207·0	0·0314	6·49
Mercury, ...	200·0	0·0319	6·38
Lithium, ...	7	0·9408	6·58
Phosphorus, ...	31	0·1740	5·39
Platinum, ...	197·4	0·0324	6·39
Silver, ...	108·0	0·0570	6·15
Sulphur, ...	32·0	0·1776	5·68
Tin, ...	118·0	0·0562	6·63
Zinc, ...	65·0	0·0955	6·20

Neumann's Law.—According to this law the specific heat of all compounds of strictly analogous composition varies inversely as their molecular weight. This law is also only an approximation, and for much the same reasons as stated in the previous paragraph, as will be seen from the following examples:—

The specific heat, in solids and liquids, also varies with the temperature, being, generally speaking, greater the higher the temperature. Finally, it also differs in different allotropic conditions of the same element, and even when the physical conditions are but slightly altered. Thus, hammered copper has a less specific heat than cast copper.

Substance.	Spec. Heat.	Substance.	Spec. Heat.
Octahedral Sulphur, . .	0·1776	Cast Copper, . .	0·0951
Prismatic Sulphur, . .	0·1844	Hammered Copper, .	0·0935

COMPOUND.	Formula.*	Molecular Weight.	Specific Heat.	Molecular Weight × Specific Heat.
Silver sulphide, . .	Ag_2S	248	0·0746	18·5
Copper sulphide, . .	Cu_2S	158·8	0·120	19·1
Sodium carbonate, .	Na_2CO_3	106	0·2728	28·9
Potassium carbonate, .	K_2CO_3	138·2	0·206	28·5
Calc-spar, . . .	$CaCO_3$	100	0·206	20·6
Spathic iron ore, . .	$FeCO_3$	116	0·182	21·1
Strontianite, . . .	$SrCO_3$	108	0·1445	21·3
Pyrolusite, . . .	MnO_2	87	0·159	13·8
Quartz, ...	SiO_2	60	0·1913	11·5
Tin-stone, . . .	SnO_2	150	0·0933	14·0

Latent Heat.—When in heating any substance, the melting or boiling point has been reached, the thermometer which previously was constantly rising, remains stationary in spite of the continued application of heat. All that the addition of heat now accomplishes, is to convert the solid into a liquid, or the liquid into a gas, at the same temperature. The heat which thus disappears and is not measured by the thermometer, is called *latent* † *heat.* This latent heat is again rendered sensible whenever the vapour or liquid respectively returns to the liquid or solid state.

To convert a kilogram of ice at 0°, into a kilogram of water at 0°, as much heat is required as would raise one kilogram of water through 79°; for, if we mix one kilogram of ice at 0°, with one kilogram of water at 79°, we obtain two kilograms of water at 0°. Hence, the latent heat of water is equal to 79 units.

By the latent heat of a liquid is meant, therefore, the heat which disappears at the moment of its assuming the liquid from the solid form, or the amount of heat required to melt a unit weight of a solid, that is, to convert it into a liquid at the same temperature. The following table gives us the latent heat of several liquids. Of all liquids water has the greatest latent heat.

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* For explanation of these formulæ, see ch. xi.

† Lateo, *I lie hid;* see also p. 40.

Latent Heat of some Liquids (Person).

SUBSTANCE.	Latent Heat.		SUBSTANCE.	Latent Heat.	
	In Units.	Water = 1.		In Units.	Water = 1.
Water, . .	79·25	1·000	Sulphur, .	9·368	0·118
Zinc, . .	28·13	0·355	Lead, . .	5·370	0·067
Silver, . .	21·06	0·265	Phosphorus, .	5·340	0·063
Tin, . .	14·25	0·179	Mercury, .	2·840	0·035

By the latent heat of a vapour is meant the heat which disappears at the moment of its formation, or the amount of heat required to convert a unit weight of the liquid into vapour at the same temperature.

The steam from one kilogram of water at 100° will raise 5·37 kilograms of water from a temperature of 0° to 100°. The latent heat of steam is therefore equal to 537 units.

The following table gives us the latent heat of some vapours. Of all vapours steam has the greatest latent heat.

Latent Heat of some Vapours.

SUBSTANCE.	Latent Heat.		SUBSTANCE.	Latent Heat.	
	In Units.	Steam = 1.		In Units.	Steam = 1.
Water, . .	536·67	1·000	Ether, . .	90·45	0·168
Alcohol, . .	208·31	0·387	Bromine, .	45·60	0·084
Acetic acid, .	101·91	0·189	Iodine, . .	23·95	0·044

Freezing Mixtures.—The action of so-called *freezing mixtures*, for the production of cold artificially, depends upon the disappearance of heat during the liquefaction of a solid or the evaporation of a liquid. The following table includes some of those more commonly known:—

Proportion by weight.	Substances Employed.	Fall of Temperature °C.
1:1	Water and Ammonium Nitrate, ...	+ 10° to — 16°
8:5	Crystallised Sodium Sulphate, and Hydrochloric Acid, .	+ 12° to — 18°
1:1	Snow and Common Salt, ...	0° to — 18°
1:1	Snow and Calcic Chloride, ...	0° to — 45°
	Ether and Solid Carbonic Anhydride, ...	0° to — 77°
	Bisulphide of Carbon and Liquid Nitrous Oxide, . .	0° to — 140°

Summary of Phenomena Observable in Connection with Change of Physical State.—Theoretically all substances are capable of assuming all three physical states, and frequently we are acquainted with a substance in the solid, liquid, and gaseous forms. Let us follow briefly the familiar instance of the conversion of ice into water, and finally into steam. Supposing the ice to be somewhat below 0°, if we heat it, its temperature will be raised (*specific heat*, p. 32) until it reaches 0°, when it will begin to melt (*melting point*). At this stage the temperature will remain stationary until all the ice is melted (latent heat, p. 34), when the temperature will again begin to rise, continuing to rise until bubbles of vapour are seen to form below the surface, which collapse again, at first, but finally rise to the surface and escape as steam (*ebullition*). At this stage the temperature will again remain constant (*boiling point*—see also latent heat, p. 35).

During all this heating some of the ice or water disappears (*evaporation*)—the rate of evaporation increasing with the temperature; and, if the experiment is conducted in a closed vessel, it will be noticed that the vapour evolved exerts a certain degree of pressure (*vapour tension*). This pressure is constant for any particular temperature, but rises with the temperature in a constantly increasing ratio, and when the temperature is reached at which the water boiled in the open vessel, the tension will be found equal to the pressure of the atmosphere.

What has here been briefly sketched in the case of water is true in the case of all solids and liquids which admit of the same transformations. It only remains to make a few further observations in connection with the above statements.

Melting Point.—By the melting point of a substance is meant the temperature at which it changes from the solid to the liquid state.* This temperature, which is constant for the same substance under the same conditions, often constitutes an important distinguishing property, and varies very considerably for different substances, as will be seen from the following selected examples :—

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* In some cases such as glass, wax, wrought iron, the change from the solid to the liquid state takes place gradually, so that for a more or less considerable range of temperature, these bodies are neither solid nor liquid, but more or less plastic; in others, such as ice, the change is abrupt.

Melting Points of some Solids.

SUBSTANCE.	Melting Point.	SUBSTANCE.	Melting Point.
Wrought iron,	1600°	Tin,	235°
Gold,	1200°	Sulphur,	115°
Copper,	1090°	Phosphorus,	44°
Silver,	1000°	Ice,	0°
Lead,	334°	Mercury,	-39°

Most substances increase in volume on melting, but some decrease. In the case of the former the effect of pressure is to raise, in the latter, to lower, the melting point.

Vapour Tension.—If a liquid is introduced into the vacuum of a barometer tube, the mercury will be more or less depressed, according to the degree of volatility of the liquid, the depression registering the elastic force of its vapour, that is the *vapour tension* of the liquid for that temperature. The amount of vapour given off from a liquid is the same, whether the space is a vacuum or not, but evaporation takes place much more rapidly in *vacuo.* Hence, the vapour tension of a liquid for any given temperature is a constant quantity. The vapour tension for all liquids at their boiling points is the same (see foregoing summary), and as these differ greatly according to the nature of the liquid, it follows that at the same temperature the vapours of different liquids exert very different pressures, as will be seen from the following examples:—

Vapour Tension of some Liquids.

TEMPERATURE.	VAPOUR TENSION IN MILLIMETRES.		
	Water.	Alcohol.	Ether.
-10°	2·093	6·50	113·2
0°	4·600	12·73	182·3
20°	17·391	44·00	434·8
34°·9	41·827	102·87	760·0
78°·4	330·0	760·0	...
100°	760·0	...	...

Boiling Point.—The boiling point of a liquid is, therefore, the temperature at which its vapour tension is equal to the pressure of the atmosphere (taken as 760 mm. bar.), and is a constant quantity for the same liquid at the same pressure, increasing with increased, and diminishing with diminished pressure.* In recording the boiling point of a liquid it is, therefore, necessary to record the pressure at which it is observed. The boiling point of a liquid at normal pressure (760 mm.) is termed its *normal boiling point.*

Normal Boiling Points of some Liquids.

LIQUID.	Boiling Point.	LIQUID.	Boiling Point.
Sulphur, . . .	440°	Benzole, . . .	80·4
Mercury, . . .	350°	Alcohol, . . .	78·4
Phosphorus, . . .	290°	Carbon Bisulphide, .	48·0
Water, ...	100°	Ether, ...	34·9

Distillation.—A liquid may frequently be purified from more or less volatile admixtures, or from solid substances held in solution, by distillation, *i.e.*, by heating it in a vessel and condensing the vapour so formed in a tube surrounded by cold water, which communicates with another vessel called the receiver, in which the distilled liquid is collected.

Sublimation.—Some substances, when heated, are converted immediately into vapour without assuming the liquid form; such substances are said to *sublime.*

Dynamical or Mechanical Theory of Heat.—According to this theory, heat is simply molecular and intra-molecular motion, and, like the motion of all material particles, can consequently be represented by its equivalent of mechanical effect or work. Thus, if the work done by the falling of one kilogram of matter from a height of 424 metres be, by suitable means, transformed into molecular motion in a kilogram of water, it is capable of raising the temperature of the water 1°C. This is called the mechanical equivalent of heat, which is expressed as 424 kilogram-metres. Conversely, the molecular energy of heat can again be converted into work, as is done, for example, in the steam-engine. Here, however, the conversion is never complete,

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* At ordinary atmospheric pressures a difference of 1 mm. in the barometric column corresponds to a difference of $\frac{1}{27}$°C. in the boiling point of water.

and could, in fact, be so only if the condenser of the engine could be kept at a temperature of—273°, the absolute zero.* But, although we cannot convert the whole of a given quantity of heat into work, we find, nevertheless, that for every unit of heat that disappears in the steam-engine as heat, 424 kilogram-metres of work are performed.

Motion, even among the free particles or molecules of gases, in relation to which condition of matter the mechanical theory of heat has been most completely investigated, may be of various kinds. It may be intra-molecular motion, *i.e.*, motion of atoms or simpler molecules within a more complex molecule, or motion of molecules as a whole, and this latter motion may be rectilinear translation or progression, oscillation, and rotation.

The progressive motion is the most important constituent of the temperature of a gas, and the *vis viva* † of this progressive motion bears, in gases, a constant ratio to the total *vis viva* of all the various motions. Now since, according to the law of expansion, the tension of a gas is proportional to the absolute temperature,* it follows that the absolute temperature must be proportional to the *vis viva* of the progressive motion of the molecules; and, further, since this *vis viva* bears a constant relation to the total *vis viva* of a gas, the absolute temperature must also be proportional to the total *vis viva* of all the various motions in the gas.‡

In a perfect gas no work is required to force the molecules asunder, since there is no cohesion to overcome. The motions of the molecules of solids and liquids are doubtless more complicated than they are in gases, and there is not the same simple relation between the *vis viva* of the various motions, but some interesting results of the theory in connection with the specific and latent heat of solids and liquids may be pointed out.

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* The tension of a confined volume of a perfect gas becomes *nil* when $1 + 0{\cdot}003665t = 0$, that is, when $t = -273°$. This temperature is called the *absolute zero*, and temperatures counted from this are called *absolute temperatures*.

† *Vis viva.* A mass projected upwards with a velocity of 32 feet per second, will rise to a height of 16 feet, or, in other words, a velocity of 32 feet per second, enables it to do an amount of work, equal to lifting its own weight, 16 feet. If now, the velocity of the mass be doubled, it will rise to 64 feet, or twice the velocity enables it to do four times the amount of work. With triple the velocity, it will do nine times the work, and with a quadruple velocity sixteen times, and so on. The energy, therefore, or capacity of doing work stored up in a moving mass, is the product of its weight and the square of its velocity divided by 64, and this is called its *vis viva*.

‡ At a temperature of 0° (273° absolute temperature), the velocities of the molecules of oxygen, nitrogen, and hydrogen, have been calculated as follows:—$O = 461$ metres; $N = 492$ metres; $H = 1{,}884$ metres, per second. The velocities of gaseous molecules are inversely proportional to the square roots of their densities.

In heating a solid or liquid, not only have all the various motions of molecules and atoms to be produced, but, as the substance expands, the molecules have to be moved further asunder against the force of cohesion; and this separation involves the performance of a certain amount of work, and, hence, expenditure of heat, just as the lifting of a weight against the force of gravity requires the performance of a certain amount of work or the expenditure of its equivalent of heat. Since temperature is governed chiefly by the *vis viva* of the progressive motion of the molecules, the heat required to produce other motions, as well as that required to force the molecules further asunder, does not appear as sensible heat, and therefore produces no effect on the thermometer. The proportion of the total amount supplied, which thus disappears, differs in different substances, and hence the varying specific heat found among solids and liquids.

As long as a substance does not change its state, the greater proportion of the heat supplied is probably converted into molecular motion. But, when a change of condition occurs, as when a solid is melted or a liquid transformed into vapour, a more or less considerable proportion of the heat supplied is required to force the molecules asunder, that is to say, it is converted into work and disappears for the thermometer; it is then said to become latent.

The heat which in either case disappears, appears again when the reverse changes are brought about. The molecules again approach each other, and in so doing, perform a certain amount of work which is converted into heat, just as the work done by a falling weight becomes, when the weight is arrested, converted into heat.

Sensible heat may, therefore, be defined as kinetic energy (energy of motion) of the molecules, latent heat as potential energy (energy of position), while specific heat is partly kinetic, partly potential.

We may, finally, consider some relations of this theory to chemical action. The heat evolved by chemical action may, in a certain sense, be looked upon as latent in the substances before union. In the act of union, the atoms or molecules, or both, lose either *vis viva*, that is, kinetic energy, or else potential energy, that is, energy of position; and the total energy of the compound kinetic and potential is less than the total energy of the uncombined components had been, and this loss is the cause of the heat evolved.

This theory also supplies a ready explanation of the fact that such chemical changes only, as are accompanied by evolution of heat, can proceed without the aid of external energy. Evolution of heat means loss of energy, loss of energy means descent from a higher to a lower level, so to speak, and this fall, when once started, is only arrested when the lowest level possible under the altered conditions is reached.

On the other hand, absorption of heat in chemical action means gain of energy, a rise in level, and this can only be accomplished by an expenditure of energy which, as it is not supplied by the combining substances, has to be supplied from without.

The following illustration may make this somewhat difficult subject clearer:—If in a structure made up of parts, a steeple built up of stones, for example, we disturb some of the lower layers, the whole structure tumbles to the ground, each individual stone seeking to gain the lowest level, or, in other words, to do the maximum amount of work of which it is capable; when once started on its downward journey, it proceeds by itself without further aid. If, on the other hand, we wish to build a steeple from a heap of stones, each stone has to be lifted to its place, that is, requires an expenditure of work upon it, and none will rise to their places without such expenditure.

CHAPTER VII.

PHYSICAL BEHAVIOUR OF SUBSTANCES TO LIGHT AND ELECTRICITY.

We must confine ourselves in this chapter to a few of the more important facts and phenomena which have a special bearing on Chemistry, dealing with them as briefly as possible, but sufficiently to explain the meaning of certain terms and numerical data which we shall find it necessary to employ in connection with the physical properties of the elements and their compounds.

A body is said to be *translucent* or semi-transparent, when it allows some of the light falling on it to pass through it; *transparent*, when it allows nearly all light falling on it to pass through it; and *opaque*, when it arrests all light, allowing none to pass through it. No substance can be said to be absolutely transparent or absolutely opaque.

Refraction.—When a ray of light passes from one medium to another of different density* (say from air into water, or *vice versâ*), it does not proceed in the same straight line, but is bent out of its course, or *refracted*.† The angle which the incident ‡ ray makes with a line, per-

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* By this term is here meant optical density, not ordinary spec. gr.

† Refractus, *broken*. ‡ Incidens, *falling upon*.

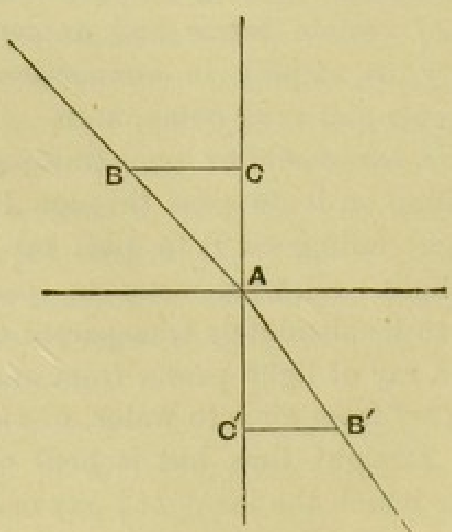
pendicular to the surface of the refracting medium, is called the angle of incidence, and the angle which the refracted ray makes with this perpendicular produced is called the angle of refraction. If the ray passes from a rarer to a denser medium, the angle of refraction is less than the angle of incidence, but if the ray passes from a denser to a rarer medium, the angle of refraction is greater than the angle of incidence. Or, in other words, in the first case the refracted ray is bent towards the perpendicular, in the second away from it. If, however, the incident ray is perpendicular to the surfaces of both media, it is not refracted, but continues in the same straight line.

Some substances possess the property of splitting the incident ray into two. Among these are calc-spar, quartz, etc. (ch. iii., p. 13). This phenomenon is termed *double refraction*.

Index of Refraction.—When, in passing from one particular medium to another, a ray is refracted, the angle of incidence bears a constant relation to the angle of refraction, such that

$$\frac{\text{sine of angle of incidence}}{\text{sine of angle of refraction}} = \text{a constant quantity.}$$

This ratio is termed the relative index of refraction, for the one medium from the other, and is very different in different substances. Thus, the relative index of refraction of glass from air is $\frac{3}{2}$; that of water from air $\frac{4}{3}$, and *vice versâ;* the relative index of refraction of air from glass is $\frac{2}{3}$, that of air from water $\frac{3}{4}$.*



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* These are approximate values. In doubly refracting substances one ray only, the ordinary ray, follows this law, the other, the extraordinary ray, follows a special law.

Take any point, B in A B, one of the sides containing the angle A, from B let fall a perpendicular, B C, on the other side A C, then $\frac{BC}{AB}$ = the sine of the angle A.

Now, if B A be the incident ray from air to water at a point A on the surface, and C A the normal to the surface, then B A C is the angle of incidence; and if A B' represent the path of the ray after refraction, B' A C' is the angle of refraction, and $\frac{B'C'}{AB'}$ is its sine. Then, whatever the angle B A C, $\frac{\sin.\ BAC}{\sin.\ B'AC'} = \frac{4}{3}$; or, if A B' be taken equal to A B, then $\frac{BC}{B'C'} = \frac{4}{3}$

since $\frac{\sin.\ BAC}{\sin.\ B'AC'} = \frac{BC}{AB} \div \frac{B'C'}{AB'} = \frac{BC}{B'C'}$.

The sine of an angle of 0 is 0; the sine of an angle of 90° is 1; and between these limits the sine increases or decreases as the angle increases or decreases.

The index of refraction, in one and the same medium, also varies with the colour of the incident light, being smallest for red and greatest for violet colour.

If the light is incident upon the substance from a vacuum, the index of refraction of the substance must be greater than 1, and is usually termed its *absolute index of refraction*,* or, simply, its index of refraction.

Total Reflection.—If a ray of light proceeding from a denser to a rarer medium, strikes the surface, separating the two media at such an angle that the refracted ray would form a right angle (or any greater angle) with the perpendicular, it cannot pass out of the denser medium, but is completely reflected at its surface. This is termed *total reflection.*

Dispersion.—It was first observed by Newton that, if a pencil of white light is made to fall upon a prism of colourless glass (or other refracting material), so as to undergo refraction, the refracted light is not white, but consists of rays of different colours, viz., red, orange, yellow, green, blue, indigo, and violet. Of these the red are least and the violet most refracted, the refrangibility of the various rays gradually increasing from the former to the latter. This decomposition of light was called by Newton *dispersion.* Not only white light but most coloured light is thus found to be compound, and to consist of rays of different refrangibility. If thrown upon a screen these colours form a band known as a *spectrum.* If the prism is held between the incident light and the eye, this spectrum is thrown on the retina.

Spectrum Analysis.—In the *spectroscope*, an instrument for examining

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* The absolute index of refraction of air is 1·000294. To find the absolute index of refraction of any substance, knowing its relative index of refraction from air, it is only necessary to multiply this last quantity by 1·000294, but the difference is very small, and may ordinarily be neglected.

spectra, the incident light is made to impinge upon the prism through a narrow vertical slit placed in the focus of a lens, and the refracted light is examined by a telescope. Not only white light, but most coloured light is thus found to consist of rays of different refrangibility. If the incandescent body be either solid or liquid, its spectrum is in nearly all cases, continuous, *i.e.*, it contains light of every refrangibility within its extreme limits. If, however, the incandescent body is a gas, its spectrum is nearly always discontinuous, *i.e.*, the light of which it consists is distributed in bright lines or bands separated by dark intervals. These bright lines or bands may include one or more colours of definite refrangibility, and in some cases are very few, in others very numerous, but, for every element they occupy, under definite conditions, definite positions in the spectrum. It is, therefore, only necessary to determine the position of the bright lines or bands in the spectrum of an incandescent gas or vapour to know at once its composition, or, at least, to recognise some element or elements contained in it. The examination of the spectra of different substances by means of the spectroscope, with the object of ascertaining their chemical composition, constitutes *spectrum analysis*.

Thus, every volatile sodium compound, if volatilised at a sufficiently high temperature, yields a spectrum consisting of two yellow lines very close to each other (so as to look like one line in spectroscopes of small dispersive power); lithium compounds yield two red lines, barium compounds a considerable number of green lines, and all these lines always occupy definite positions in the spectrum.

The number of elements or their compounds that can be volatilised in an ordinary non-luminous flame, such as a Bunsen burner, is small, but it includes some of the most widely diffused metallic compounds such as those of sodium, potassium, lithium, calcium, etc. In the intense heat of the electric arc, or of a powerful electric spark, nearly all substances, however, can be volatilised, and made to yield a spectrum. But, at that intense heat the spectra frequently differ from those obtained at lower temperatures, the difference being probably due to decomposition. Generally speaking, at lower temperatures, the spectrum consist of bands, at higher temperatures, of lines.

The delicacy of the spectrum reaction of some of the elements is almost inconceivably great; thus, $\frac{1}{100,000,000}$ of a grain of sodium, or $\frac{1}{7,000,000}$ of a grain of lithium can be recognised with absolute certainty when introduced into the flame of a Bunsen burner on a fine platinum wire. In consequence of this exceeding delicacy, not only have known elements (such as lithium, for example) been shown to be far more widely diffused than was previously imagined, but a number of new elements have been discovered by its means.

But spectrum analysis has done more than this—it has enabled the chemist and astronomer to analyse the nebulæ, the luminous atmospheres of the sun and stars, and in fact every luminous vapour the light from which is visible in our telescopes. It would lead us too far to go fully into this matter, and we must, therefore, refer the student to special works on the subject for fuller information. A few general principles may, however, be given. According to Kirchhoff, every incandescent substance absorbs that particular kind of light which, under the same conditions of temperature, it is capable of emitting. If, therefore, we allow a very intense light from a source yielding a continuous spectrum, to pass through a gas or vapour of lower luminosity, the gas or vapour will absorb precisely that portion of this light which it is itself emitting, while all other portions pass through unaltered. As a consequence of this, the transmitted light is deficient in those rays which the luminous gas or vapour has absorbed; and, when now examined by a spectroscope, those parts of the spectrum corresponding in refrangibility with the light emitted by the luminous gas or vapour, will appear dark by contrast with the other and intensely bright portions ; the line or lines previously bright on a dark back-ground will now appear dark on a bright back-ground. It is owing to this reversal, without change of position, of the luminous lines which the atmospheres of the sun and stars themselves would yield that their composition can be determined.

Many coloured media absorb light of definite refrangibility, and, accordingly, when interposed between a white light and the slit of the spectroscope, blot out certain definite portions of the previously continuous spectrum, thus producing dark lines or bands in the otherwise bright spectrum. These lines or bands, the position of which is definite for definite conditions, and which are termed *absorption spectra*, may also frequently be made use of for the detection of certain substances, more particularly coloured substances, in solution or otherwise.

Thus, spectrum analysis, the discovery of Bunsen and Kirchhoff, by means of which the composition of a substance may be determined from an examination of its incandescent vapour through a glass prism, has become a powerful agent of discovery in the hands of the chemist, and has shown that the material of his study is only limited by the visible universe.

Colour.—From what has been said in the previous paragraph, it will be seen, that the phenomenon of *colour* is obviously due to a partial absorption of the components of white light. Colour often forms an important distinguishing property of a substance.

Physical Behaviour of Substances to Magnetism and Electricity.—In connection with the subjects of magnetism and electricity, the following definitions will suffice:—Substances are said to be *magnetic* (*or paramagnetic*), when attracted, and *diamagnetic*, when repelled, by a magnet.

Some substances, when rubbed with cloth, flannel, silk, &c., become *electrically excited* (sulphur, glass, &c.)—*i.e.*, they develop the temporary power of attracting light bodies. Substances are said to be *non-conductors* of electricity, if, when electrically excited, they do not allow the electric fluid to spread over their whole surface, or if they refuse to allow an electric current to pass through them. On the other hand, they are called *conductors*, if, when electrically excited, they allow the electric fluid to spread over their whole surface, or if they permit an electric current to pass through them.

Metals are among the best conductors of electricity as they are of heat, and a remarkable relation exists between their conducting powers for heat and electricity, viz., that these are (approximately) directly proportional to one another, as will be seen from the following table in which silver is taken as the standard in both cases:—

Relative Conductivity of some Metals for Heat and Electricity.

METAL.	CONDUCTIVITY.	
	For Heat.	For Electricity.
Silver, ...	100	100
Copper, ...	73·6	77·43
Gold, ...	53·2	55·91
Tin, ...	14·8	17·0
Iron, ...	11·9	14·4
Lead, ...	8·5	7·7
Platinum, . . .	8·4	10·53
Bismuth, . . .	1·8	1·19

CHAPTER VIII.

SPECIAL PROPERTIES OF SOLIDS, LIQUIDS, AND GASES.

Cohesion.—By *cohesion* is meant the force of attraction exerted between the molecules of a solid or liquid. In a gas this force is absent. This force of cohesion, as already stated (p. 11), is greater in solids than in liquids, but varies considerably in different solids and liquids. The following definitions will suffice to illustrate this variation in the case of *solids* :—

Malleability.—A solid is said to be *malleable* when it can be hammered or rolled out into plates—*e.g.*, gold, wrought iron, copper, lead, &c.

Ductility.—A solid is said to be *ductile* when it can be drawn out into threads or wire—*e.g.*, plastic sulphur, copper.

Brittleness.—A solid is said to be *brittle* when it breaks readily under a blow or under pressure—*e.g.*, bismuth, glass.

Elasticity.—A substance is said to be *elastic* when, after stretching or bending, it tends to return to its original form—*e.g.*, india-rubber, steel. Elasticity is often combined with brittleness—as in glass.

The fact, that liquids are capable of assuming the form of drops, indicates that *cohesion* is by no means absent from their molecules, but that this cohesive force varies considerably in different liquids, is a matter of common observation. A liquid possessing great mobility of particles is said to be *limpid*—*e.g.*, ether, alcohol, turpentine. If, on the other hand, its particles move slowly and with difficulty, it is said to be *viscous*, *e.g.*, glycerine.

Adhesion.—The term *adhesion* refers to the force of attraction often exerted between the particles of different solids, or between solids and liquids. The action of glue, gum, cements, &c., is due to *adhesion*.

Diffusion of Liquids.—Liquids which are miscible, will, when superimposed, or brought otherwise into contact, gradually interpenetrate each other, even when differing greatly in density.

For example, strong sulphuric acid of specific gravity 1·8 (coloured with indigo to make it more visible) if introduced carefully into a cylinder of water, by means of a thistle funnel, so as to form a separate layer at the bottom, will, in the course of a few weeks, gradually mix itself with the water, and the final result will be the same as if the two liquids had been shaken together. This phenomenon is termed *diffusion*. If a solution of a substance is put into a vial so as to entirely fill it, and this vial is itself immersed in a large beaker containing pure water, in such a manner, that the mouth of the vial is covered by the water, the substance contained in solution diffuses from the vial into the water of the beaker, and the amount so diffusing can readily be estimated. This amount depends on the character of the substance in solution, its concentration and its temperature and upon the size of the mouth of the vial, increasing with the increase of the latter three items. From a solution containing 20 parts of substance, to 100 parts of water, at a temperature of 60·5°F., the following amounts diffused out of the vial in eight days:—sodium chloride, 58·68 grains; sodium nitrate, 51·56 grains; magnesium sulphate, 27·42; cane sugar, 26·74; gum arabic, 13·24; albumen, 0·38 (vial diffusion—Graham).

Substances thus differ greatly in the rate at which they diffuse into water, and may, to a certain extent, be even separated one from the other by diffusion. In some cases this difference in rate even brings about chemical decomposition, as when a solution of alum is made to diffuse into water, the sulphate of potassium diffuses more rapidly than the sulphate of alumina.

*Osmosis.**—Diffusion will also take place when the liquids are separated by a membrane such as a bladder, under which circumstances it becomes evident that some liquids diffuse much more rapidly than others. The phenomenon is known as osmosis.

Dialysis.†—A crystalline salt in solution will also diffuse through the combined water of certain other substances, as readily almost as it diffuses into water; as, for example, into a jelly, while substances which gelatinise (or *pectise*, as Graham called it), do not do so at all, or very slowly. Graham suggested the term *crystalloids* for the former class, and *colloids* ‡ for the latter class of substances. Use is frequently made of this peculiar property of crystalloids and colloids to separate or purify them, and the process is termed *dialysis*.

In dialysis, the solutions to be dialysed are placed in a shallow vessel, the bottom of which is made of a colloid membrane, usually parchment paper, and this vessel is floated on, or suspended in, another vessel containing pure water. Crystalloids are capable of diffusing through the combined water of the colloid membrane, and then into the water beneath—colloid substances cannot do so.

Dialysis plays an important part in the distribution of solids, liquids, and gases, in the animal body, as in respiration, digestion, etc. An excellent illustration is afforded by the behaviour of blood-corpuscles to water. The blood-corpuscles, when floating in the serum of the blood, have a definite shape, depending on the rate at which diffusion or dialysis takes place from the serum into the corpuscle, and *vice versâ*. If we disturb the established equilibrium, as, for example, by adding water to the serum, more water diffuses or dialyses into, than out of,

* ὠσμός, *an impulse.* † διὰ, *asunder;* λύσις, *separation.* ‡ κόλλη, *glue.*

the corpuscles, and they burst. But if we add salt, the reverse action occurs, and they shrink. When examining blood-corpuscles we must place them, therefore, in a medium resembling blood-serum.

Solution.—All gases and some liquids are miscible with one another in all proportions; all gases are absorbed in greater or less quantity by water or other liquids; some liquids are only partially miscible with one another; most solids in contact either with water or some other liquid assume the liquid condition; in all the above cases the resulting mixture is called a *solution*. A solution is, therefore, *a homogeneous mixture of heterogeneous molecules*, which allows no separation of its constituents by mechanical means. The solution of solids and their separation from solution show great similarity to the processes of evaporation and condensation. (See also p. 61.)

This dissolving power of water and other liquids is limited, both as regards quantity and quality of substances brought into contact with them; that is to say, some substances are not soluble (*insoluble*) in certain liquids, and of those which are soluble, some are more so than others, and in nearly all cases a point is reached beyond which further solution is impossible. A liquid which contains the greatest possible amount of the substance which it can hold in solution at a given temperature is said to be *saturated*.

It is usual to distinguish between *ordinary solution*, whereby the nature of the dissolved substance remains unchanged (as, for example, common salt in water), and *chemical solution*, whereby the dissolved substance undergoes a change of nature in the act of solution (as, for example, copper in nitric acid); but there is no real difference in these cases, as regards the process of solution, since, in the latter case, the substance is first acted upon chemically by, and finally dissolved in excess of, the solvent.

In the case of solution of solids unaccompanied by any chemical action, a fall of temperature generally takes place; if chemical action occurs, a rise of temperature takes place, and this also happens when chemical action occurs between miscible liquids, or between liquids and gases which are soluble in them.

As a general rule, but not always, solids are more soluble at higher than at lower temperatures. In the case of gases the solubility decreases as the temperature rises, so that (with few exceptions) a gas can be expelled from its solution by heat.

Coefficient of Solution of Gases.—The solubility of a gas, at least in gases of moderate solubility, increases as regards *weight* directly with the pressure exerted by the gas, and hence the *volume* dissolved is always the same for the same temperature. Hence, in a mixture of gases the amounts dissolved are proportional to the volume of each gas present in the mixture. The volume of a gas which is dissolved by the unit volume of any liquid at a given temperature and pressure (usually 0° and 760 mm., Bar.), is called its *coefficient of solution*, or *absorption*.

Diffusion of Gases.—If two liquids of different density, which are not miscible, in the strict sense of the word, be shaken together, they will more or less quickly separate into two layers, the lighter liquid forming a layer above the heavier one. But all gases are completely miscible with one another, whatever be their difference in density, and if mixed, will not again separate into layers, as in the case of liquids. Moreover, complete admixture will take place when gases are brought into contact with one another, even against the action of gravity. If, for example, a bottle filled with the very light hydrogen gas be inverted and connected with a bottle filled with the heavy carbonic acid gas, below it, these two gases will, in a few hours, be found to be completely mixed in both vessels. This diffusion will also take place, even when the gases are separated by a partition of a porous material, such as plaster of Paris, or unglazed earthenware. The diffusion of gases, however, takes place at very unequal rates, depending on the density of the gas. The rates of diffusion, in fact, vary inversely as the square roots of their densities; thus, hydrogen (density 1) will diffuse four times as rapidly as oxygen (density 16). *

There is also a kind of diffusion of gases corresponding to the process of dialysis in liquids. That is, some gases have the power of uniting with, or diffusing into, a solid entirely devoid of pores, and escaping again on the other side of the solid in contact with a different gas, as *e.g.*, carbonic acid and oxygen passing through a diaphragm of india-rubber, or hydrogen passing through iron or palladium. It has been suggested by Graham that this species of diffusion is due to actual liquefaction of the gas at the surface of the solid.

Behaviour of Gases to Pressure—Boyle's Law.—The volume of a gas varies inversely as the pressure to which it is subjected. If V = volume at pressure, P and v = volume at pressure p, then—

$$V : v : : p : P ;$$

hence, also the tension or elastic force of a gas varies directly as the pressure to which it is subjected. For example, a gas measured at the ordinary atmospheric pressure (760 mm., Bar.) is reduced to $\frac{1}{2}$ its volume, and its tension doubled by a pressure of 2 atmospheres, or to $\frac{1}{x}$th its volume, with tension $= x$ at x atmospheres.

This law is not absolutely but only approximately true for the less

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* This is strictly true only when diffusion takes place through a minute hole in a very thin plate.

easily condensible gases, but for ordinary calculations relating to change of volume, corresponding to barometric variation, it is sufficiently accurate, for practical purposes, for all gases.

Normal Volume of Gases.—By the normal volume of a gas is meant its volume at 0° and 760 mm., B. In order to calculate this volume for purposes of comparison for any gas of observed volume at observed temperature and pressure, it is necessary to combine the above formula (Boyle's law) with the formula for calculating variations in volume due to temperature only (see ch. vi., p. 29).

Thus :—

If $V_{p't'}$ = vol. at required temperature t' and pressure p',
and V_{pt} = vol. at observed temperature t and pressure p,

$$\text{then } V_{p't'} = \frac{V_{pt} \times (273 + t')}{273 + t} \times \frac{p}{p'}.$$

And this formula holds good for all cases where change of volume, due to change of temperature and pressure, has to be calculated.

Liquefaction of Gases.—There is no absolute distinction between gases and vapours, beyond the fact that, by a *vapour* is meant the gaseous form of a substance which is liquid at ordinary temperatures, whereas, by a *gas* is meant the gaseous form of a substance which is only liquid at low, or very low temperatures. Just as vapours may be condensed to the liquid form by cooling, so many gases under the same circumstances may be made to assume the liquid state, the difference being that, usually in the latter case, a much lower temperature is necessary. Not all gases can, however, be thus liquefied, but most of them can be condensed to liquids, even at ordinary temperatures, by the application of more or less considerable pressure, while all gases, with the exception of hydrogen, yield to the combined effect of cold and pressure.

Up to the year 1877, five gases—oxygen, hydrogen, nitrogen, carbonic oxide, and marsh gas had resisted all attempts to liquefy them, even at extremely low temperatures, and enormous pressures exceeding (at least in the case of oxygen and hydrogen) 3000 atmospheres. A discovery of Andrews, however, viz., that for every gas there was a temperature (termed by him the *critical point*), above which no amount of pressure was sufficient to liquefy it, made the condensation of these gases simply a question of temperature, and they have now all, with the exception of hydrogen, been condensed at pressures, in most cases below, or not much exceeding 300 atmospheres.

CHAPTER IX.

CONDITIONS FAVOURING CHEMICAL ACTION.

We have already learnt (ch. i.) that elements are capable of uniting with each other to form compounds, and we shall further learn that many compounds in their turn are capable of uniting with other compounds or with elements. We have now to consider more fully the conditions, qualitative as well as quantitative, which govern these combinations.

A.—*Influence of Physical State.*

Since chemical action can only take place between different substances when there is intimate contact, the smallest appreciable space rendering chemical action impossible, all conditions which favour intimate contact also favour chemical action. Accordingly, we find that, as a rule, the liquid state in the case of at least one of the acting substances is the most favourable, and, if it is desired to bring about chemical action between two or more substances, one of these at least should, if possible, be brought to this physical state. This can be done either by heating the solid so as to melt it, or by dissolving it in a suitable liquid. If one of the acting bodies be a solid, much depends upon its mechanical condition; if it be a dense compact mass chemical action is slow, but increases in rapidity with the degree of division. Thus, iron, which in a compact mass is permanent in dry air, and practically incombustible, takes fire spontaneously, as soon as it comes into contact with air, when in a very fine state of division, as obtained by reducing ferric oxide with hydrogen at a low temperature.

Action between solid and solid.—This is, strictly speaking, probably impossible, though a few phenomena are known which, at first sight, seem to indicate its possibility. Thus, phosphorus and iodine readily unite at ordinary temperatures, and iron filings and sulphur, when mixed, unite readily, when the mixture is moistened with water, in which neither of these two substances is known to be soluble.

Action between solids and liquids.—This is as above stated, very common.

Action between solids and gases.—This is also not unfrequent, since the particles of a gas readily admit of being brought into intimate contact with a solid; among numerous examples we may mention the burning of iron or carbon in air, copper in sulphur vapour, antimony in chlorine, &c.

Action between Liquids and Liquids.—Liquids are for the most part readily miscible; their particles are thus easily brought into the necessary contact, and chemical action, as a rule, therefore, takes place most readily between them.

Action between Liquids and Gases.—All gases are more or less soluble in many liquids, or, in other words, are readily brought into intimate contact with them; hence, action between liquids and gases is not uncommon.

Action between Gases and Gases.—All gases can be mixed with each other, and chemical action between them is by no means infrequent, in spite of the fact that the absence of cohesion between their particles tends to keep them asunder.

B. Other Special Conditions.

Action of Heat.—In the great majority of cases, substances have to be heated to a greater or less degree, before they begin to unite, while, on the other hand, a high temperature destroys most or all chemical compounds. As a rule, a moderate temperature favours, a high temperature prevents, chemical combination.

Action of Light.—Light, like heat, sometimes favours chemical combination, sometimes decomposition. Thus, chlorine and hydrogen, when kept at ordinary temperatures in the dark, do not unite; if, however, they are exposed to light, they at once begin to unite, the rapidity of union being the greater, the greater the intensity of the light; and in direct sunlight, in the electric light or in the light produced by burning magnesium, they unite instantaneously with explosion. On the other hand, the halogen compounds of silver,* for example, are decomposed by exposure to light, the more rapidly the more intense the light, and this fact finds its application in photography. Under the influence of sunlight the green parts of plants decompose carbonic anhydride, oxygen being given off and the carbon assimilated.

Action of Electricity.—Electricity also sometimes favours chemical union, but more frequently brings about decomposition. Thus, under the influence of a series of electric sparks, nitrogen, oxygen, and water-vapour unite to form nitric acid, and various gases may be made to combine under the influence of the so-called silent discharge; on the other hand, many gaseous compounds are broken up by a series of

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* Silver compounds of chlorine, bromine, or iodine.

electric sparks, and most chemical compounds are decomposed, if a powerful electric current be passed through them.

Influence of Contact.—In some cases the mere presence (even in small quantity) of a certain substance seems sufficient to induce chemical action between others, action which but for its presence would not have taken place, and as in the case of heat, light, and electricity, this cause sometimes favours combination, sometimes decomposition. Thus, many gases and vapours unite with oxygen at ordinary or but slightly elevated temperatures in the presence of platinum, and the more rapidly the more finely divided the platinum is. On the other hand. potassium chlorate loses its oxygen much more rapidly in the presence of manganese dioxide than when alone, hydric peroxide parts with its oxygen in the presence of manganese dioxide or of metallic silver, &c. These and similar phenomena are supposed by some to be due to a peculiar influence exerted by the substances in question, called catalytic[*] action. In most, if not in all cases, this action can, however, be explained as due to ordinary mechanical or chemical causes.[†]

Nascent State.[‡]—In many cases elements or compounds, at the moment of their liberation from combination, possess much more active properties than when in their ordinary condition. Thus, hydrogen passed through a solution of ferric chloride has little or no action on it, but, when generated in the solution itself, reduces it to ferrous chloride; again, silver chloride suspended in water is not acted upon by free hydrogen, but is rapidly reduced to metallic silver with formation of hydrochloric acid by hydrogen liberated in the liquid in which it is suspended.

All these phenomena find ready explanation in the assumption that elements in the free condition nearly always consist of molecules formed by the union of two or more atoms; hence, their affinities are, to a certain extent, satisfied, and in order to produce chemical action this molecule has first to be decomposed. When, however, an atom is liberated from a compound it may, for an instant at least, be conceived to be unfettered by union with another atom, and hence, its whole chemical energy is free to act, and it can readily be understood that under such circumstances it would be more powerful to effect chemical action.

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[*] κατάλυσις, *an unloosing.*

[†] The action of platinum is probably due to the condensation of the gases on the surface of the metal whereby the molecules are brought into more intimate contact, heat being simultaneously produced by the condensation; both these effects favouring chemical action. The effect of manganese dioxide on chlorate of potassium is probably due to the alternate oxidation of the dioxide by the chlorate and the decomposition of this higher oxide by heat. Irrespective of this, however, the presence of a third substance appears to be necessary in many cases to enable two other substances to act chemically on each other. Thus, pure zinc is less readily soluble in acids than impure zinc, pure nitric acid acts far less readily on metals than acid containing nitrous acid, notably in the case of copper. Again, perfectly dry phosphorus does not burn in perfectly dry oxygen, and a perfectly dry mixture of carbonic oxide and oxygen cannot be exploded by the electric spark.

[‡] Nascor, *I am born.*

CHAPTER X.

ATOMS AND MOLECULES.

Observed Laws of Chemical Combination.— Having in the previous chapter reviewed the various conditions which favour chemical action, we must next turn our attention to the quantitative considerations involved. In the first place, a given compound is always composed of the same elements, however and wherever it may be produced. Thus, water is always made up of oxygen and hydrogen, common salt of sodium and chlorine. But by a compound is meant much more than this, as will be seen from the following laws deduced from actual observation :—

1. **Law of Fixity of Proportions.**—*In a compound the elements composing it are always united in the same proportion by weight.* Thus, water is not only always composed of oxygen and hydrogen, but these elements are in water always united in the proportion of 2 parts by weight of hydrogen to 16 parts by weight of oxygen. Common salt is always composed of sodium and chlorine, and always of 23 parts by weight of sodium and 35·5 parts by weight of chlorine.

2. **Law of Equivalent Proportions.**—*The proportion in which two elements unite with the same weight of a third element, is generally also the proportion in which they unite with each other* (or stands in some simple relation to these latter quantities).

Thus, if xA and yB unite with zC, then if A and B unite with one another, they unite in the proportion of xA to yB (or 2 xA to 3 yB, &c.).

Thus, 71 parts by weight of chlorine unite with 56 parts by weight of iron, to form ferrous chloride, or with 16 parts by weight of oxygen to form hypochlorous anhydride, and iron and oxygen unite with each other in the proportion of 56 to 16 parts by weight respectively, to form ferrous oxide, or also in the proportion of 112 parts (twice 56) of iron to 48 parts (thrice 16) of oxygen to form ferric oxide, and so on.

3. **Law of Multiple Proportions.**—*If two elements unite with one another in several proportions, then the quantities of the one element which unite with the same weight of the other are generally simple multiples of a common factor.*

Thus, nitrogen and oxygen unite with each other in five different proportions, viz. :—

In *nitrous oxide* 28 parts by weight of nitrogen are united with 16 parts by weight of oxygen ;

In *nitric oxide* 28 parts by weight of nitrogen are united with 16 × 2 parts by weight of oxygen ;

In *nitrous anhydride* 28 parts by weight of nitrogen are united with 16 × 3 parts by weight of oxygen ;

In *nitric peroxide* 28 parts by weight of nitrogen are united with 16 × 4 parts by weight of oxygen ;

In *nitric anhydride* 28 parts by weight of nitrogen are united with 16 × 5 parts by weight of oxygen.

Copper and sulphur unite in two different proportions with each other, viz. :—

In *cupric sulphide* 32 parts by weight of sulphur are united with 63·5 parts by weight of copper ;

In *cuprous sulphide* 32 parts by weight of sulphur are united with 63·5 × 2 parts by weight of copper.

These laws, as thus stated, are simply expressions of observed facts ; they do not involve any theoretical speculations whatever, and remain true, whatever the attempted explanations may be. It is highly important to bear this in mind, and clearly separate here, as elsewhere, observed facts from their attempted explanation.

Atomic Theory.—The now almost universally accepted explanation of these laws of combination by weight, first originated with Dalton in 1803, in his celebrated *Atomic Theory.* According to this theory all matter is made up of minute particles or atoms (ch. ii., p. 10).* These atoms are indivisible and unalterable. All atoms of the same element are exactly alike in all respects, but there are more or less considerable differences between the atoms of different elements.

On these assumptions it becomes easy to understand why elements unite only in certain fixed proportions, and why always in the same proportions, these being nothing more nor less than the relative weights of their atoms. The law of multiple proportions finds also in this theory a ready explanation, for, if one element unite with another in several proportions, these proportions are determined by the combinations of 1, 2, 3, 4, &c., atoms respectively, and no compound is possible which contains any other proportions, such as would corre-

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* Ideas on the atomic constitution of matter are to be found in the writings of the philosophers of ancient Greece, but these ideas were first applied to the explanation of chemical combination by Dalton.

spond to half or quarter atoms, &c., since these, according to the theory, are impossible.

Atomic Weight.—By atomic weight is meant the relative weight of the atoms of the different elements, that of hydrogen being taken as unity. From what has just been said, and from the statement of the three laws of combination by weight, it might be supposed by some that the relative weights of the atoms of all the elements were either identical with the proportions in which they combined, or that they might easily be inferred from these proportions; but a little consideration will show that, as we are unable to deal with individual atoms, or even count the number of atoms contained in the molecule of any compound by direct observation, something further is necessary to fix these atomic weights. For example, hydrogen unites with oxygen in two different proportions, viz.:—

1 part by weight of hydrogen unites with 8 parts by weight of oxygen to form *water;*

1 part by weight of hydrogen unites with 16 parts by weight of oxygen to form *peroxide of hydrogen.*

Now, which two of these three numbers are to be taken as expressing the relative weights of the atoms of hydrogen and oxygen? Is the weight of the oxygen atom 8 times that of a hydrogen atom, and have we in a molecule of the first compound 1 atom of hydrogen united with 1 atom of oxygen, and in the second 1 atom of hydrogen to 2 atoms of oxygen? Or, is the weight of an atom of oxygen 16 times that of an atom of hydrogen, and have we in a molecule of the first compound 2 atoms of hydrogen to 1 atom of oxygen, and in the second 1 atom of hydrogen to 1 atom of oxygen? By the mere quantitative analysis of these compounds we cannot answer these questions. It becomes, therefore, clearly necessary to have recourse to some other guide in deciding the atomic weights of the elements, and we are in fact obliged to resort once more to theory.

But, before describing the methods in general use for fixing the atomic weights of the elements, it is very necessary to clearly apprehend what the unit of matter is with which the chemist has, as a rule, to deal.

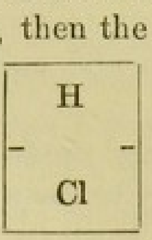
Except in a very few instances, and whether we are dealing with elements or with compounds, this unit is not the atom, but the combination of two or more atoms called a molecule (ch. ii.). Atoms, with few exceptions, are known only in combination; it is the molecule which is known in the free state. We have, therefore, in the first place, to fix the weight of the molecule (*molecular weight*), and having done that, we can deduce the weight of the atom (*atomic weight*).

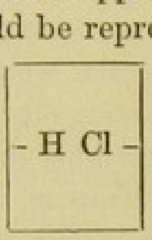
Molecules are individually so excessively minute (p. 11), that even if we could isolate one we should not be able to weigh it, neither can we take the weight of a thousand, or a million, or indeed of any particular number of molecules, since we have no means of counting them.

All we can do is to obtain their relative weight. In order to effect this, it is only necessary to find a measure such that, whatever the actual number of molecules may be which it will hold, it will always hold the same number, irrespective of the substance put into it. Avogadro has supplied us with this necessary measure, for, according to his law,[*] *equal volumes of all gases and vapours under like conditions of temperature and pressure contain the same number of molecules* (independent particles); or, in other words, the relative weights of equal volumes of any gases or vapours, when measured under like conditions of temperature and pressure, are also the relative weights of the molecules of these gases and vapours.

Our so-called molecular weights, therefore, do not represent the absolute weight of a molecule or of any particular number of molecules; they are merely relative weights—they tell us how many times heavier a molecule of any element or compound is than an atom of hydrogen, which, being the smallest proportion of matter known to exist in any molecule, has been taken as the unit.

This law proves irresistibly the statement made at the beginning of the chapter, viz.:—That, except in a very few instances, and whether we are dealing with elements or with compounds, the unit with which we deal is not the atom but the molecule. An example may make this important fact clearer:—1 volume of hydrogen unites with 1 volume of chlorine to form 2 volumes of hydrochloric acid. Assuming the composition of hydrogen and chlorine to be atomic, and supposing each atom to occupy 1 volume, then the above result could be represented thus:—





This is, however, manifestly not the correct representation, if Avogadro's law be true, for, in the two volumes of the mixed gases

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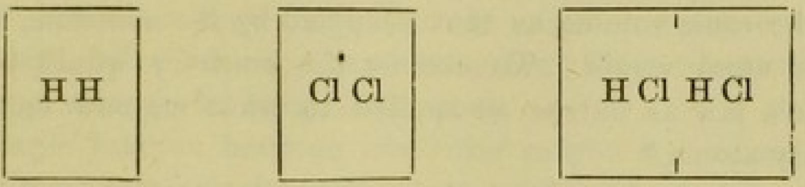
[*] This law is justifiable for various reasons based on the mechanical theory of heat which would lead us too far for our present purpose, but it may be mentioned that the following facts are explicable on the assumption that all gases have a similar molecular constitution (Avogadro's law), viz.:—That all gases behave sensibly alike to variations of temperature and of pressure, and that the mixture of two gases which have no chemical action on one another, is unaccompanied by change of temperature.

before union, we have two independent particles, but in the two volumes after union only one, whereas Avogadro's law requires the presence of an equal number of independent particles in equal volumes. The correct representation would, therefore, be as follows :—



We have now in the mixed gases before union two independent particles, viz. :—1 molecule of hydrogen, and 1 molecule of chlorine, and after union also, two independent particles, viz. :—2 molecules of hydrochloric acid. A similar train of reasoning leads to the conclusion that the other elements consist, with few exceptions, of two-atom molecules.

Our standard of measure is, therefore, the molecule of hydrogen; and the next question is what numerical value are we to give to it? As previously shown (page 58), assuming Avogadro's law to be correct, it follows that a particle of free hydrogen, as we know it, must be made up of at least two distinct, but similar sub-particles, which, in the free hydrogen are united and form what we call the molecule of hydrogen. Now, when a molecule of hydrogen is chemically acted on by other molecules, the hydrogen sub-particles are caused to separate and combine with the other, and dissimilar sub-particles of these molecules to form new molecules, no longer hydrogen, nor, indeed, elementary in their character, but compound, for example:—When a molecule of hydrogen is acted on by a molecule of chlorine the hydrogen sub-particles separate and unite each with a sub-particle of chlorine to form two molecules of hydrochloric acid.

The free particle, or molecule, of hydrogen is, therefore, divisible into two parts, but, so far as we know at present, no further, and one of these parts, or sub-particles, as we have termed them, is accordingly called the atom of hydrogen, and is taken as our unit of weight in expressing the atomic or molecular weights of other elements or compounds. The molecule of hydrogen, as above defined, will, therefore, weigh two such units. The next question is—What volume are we to assign to this molecule? The simplest assumption would seem to be to call the volume occupied by this molecule unity. This, however, has not been done; firstly, because confusion might arise if our standard were taken as representing two units of weight and only one unit of volume; and, secondly, because there seems to have been some confusion in the minds of many chemists in regard to the volume occupied by the molecule and atom respectively. It seems to have been assumed that because the molecule of hydrogen has twice the weight of the atom of hydrogen, that it also must occupy twice the volume. This, however, was obviously a misapprehension, and there can be no doubt that if we could obtain hydrogen in the atomic form its atom would occupy the same volume as that occupied by the molecule, as, indeed, any other atom would. To assume the contrary would be to take Avogadro's law as untrue as applied to what we now believe to be elementary atoms.*

We know, indeed, at least three elements, namely—mercury, zinc, and cadmium, in the atomic condition; and in these the atoms occupy the same volume as that occupied by the molecule of other elements.†

Be this, however, as it may, the weight of a molecule of hydrogen is taken as weighing two units and the volume it occupies as two unit volumes; and we call *the weight of any gas or vapour which, under like conditions of temperature and pressure, occupies the same volume as two parts by weight of hydrogen, the molecular weight of the substance from which this gas or vapour is derived.* Or, in other words, the molecule of any substance, in the state of gas or vapour, is assumed to occupy two volumes like the molecule of hydrogen as above defined.

This unit of measure is twice that taken for estimating the specific gravity of gases and vapours, and hence it follows that in order to obtain the molecular weight of a substance from the specific gravity of its gas or vapour as compared to hydrogen we must multiply this specific gravity by 2.

$$\text{Spec. gr.} \times 2 = \text{molecular weight.}$$
$$\text{Molecular weight} \div 2 = \text{spec. gr.}$$

The volume thus assumed to be occupied by molecules is obviously not even the relative space occupied, or filled, by the actual substance of the various molecules in the sense, for example, implied in the statement that a kilogramme of water occupies, or fills a volume of 1 litre, but it is the volume occupied by the actual substance of the molecule plus the free space in which the molecules move.‡ This free

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* This *atomic hydrogen* would be the most logical unit, not only as regards atomic and molecular weights, but also as regards specific gravity. The specific gravity of ordinary *molecular hydrogen* would then be 2, and the specific gravity of any gas or vapour would then directly express its molecular weight.

† To these we may probably add potassium and sodium and some others.

‡ Better still, perhaps, it would be not to speak at all of the volume occupied by the atom or molecule, of which we know nothing, but to speak always of the volume occupied by atomic or molecular proportions of the various elements and compounds. This, however, would involve a considerable change in our ordinary chemical language as we then ought never to speak of atoms or molecules, but only of atomic or molecular proportions. It will, therefore, be sufficient for the student to remember that our so-called atomic or molecular volumes are really the volumes occupied by atomic or molecular proportions of the elements or compounds.

space is, relatively, enormously great in the case of gases and vapours; it is far smaller in the case of liquids and solids. We may compare this molecular occupation of space with that of a country said to be occupied by an army; the actual extent of ground covered by the individual soldiers is very small, but the whole country is within the sphere of activity of the army; and the greater this activity the greater the extent of country the army can occupy.

This simple relation between molecular weight and specific gravity enables us readily to calculate the actual weight of any given volume of any gas or vapour provided only that we remember the molecular weight of the substance from which the gas or vapour is derived, and the actual weight of any definite volume of any gas or vapour. The substance naturally chosen for this latter purpose is hydrogen. The first definite constant proposed is the crith of Prof. Hofmann. A crith is the weight of 1 litre of hydrogen measured at 0° and $760^{m.m}$ pressure, and is equal to 0·0896 gramme. The second constant in use is that proposed by Prof. Williamson, viz., the weight of 11·19 litres hydrogen, which, when measured at 0° C. and $760^{m.m}$ pressure (32° F. and 30 inches), weigh 1 gramme. The weight of 1 litre of any gas or vapour measured at the standard temperature, and pressure is, therefore, 1 crith (0·0896 gramme), multiplied by one half the molecular weight of the gas or vapour; or the weight of 11·19 litres of any gas or vapour measured at the standard temperature, and pressure is equal to one half the molecular weight expressed in grammes. Thus—

$$1 \text{ litre } C\,O_2 = 0{\cdot}0896 \times 22 = 1{\cdot}9712 \text{ grammes;}$$
$$\text{or } 11{\cdot}19 \text{ litre } C\,O_2 = 22 \text{ grammes.}$$
$$\text{Molecular weight of } C\,O_2 = 44.$$

In cases in which Avogadro's law is not available Raoult's proposition or law may frequently supply the deficiency. The law may be stated thus:—Solids or liquids dissolved, in molecular proportions, in a solvent on which they have no chemical action, produce equal depressions in the vapour pressure or freezing point of the solvent. Or the depressions produced by 1 gramme of substance in 100 grammes of solvent, are to each other inversely as the molcular weights of the substances dissolved. The molecules of a solid or liquid, when dissolved in an inert solvent may be assumed to be, in some measure, in the condition of a gas. Like the molecules of a gas they tend to separate from each other to the greatest extent possible. A solution, however dilute, is of the like composition in every part; hence, solutions, like gases, show similarities in their behaviour. The more dilute the solution the greater the resemblance to a perfect gas.

Determination of Atomic Weights.—Having now considered the means of fixing the weight of the molecule, that portion of matter with which the chemist has, as a rule to deal, let us return to the consideration of atomic weight. The considerations which chiefly guide the chemist in fixing the atomic weights of the elements are:—

1. *The atomic weight must represent the smallest quantity of an element which can be contained in any molecule;*

2. *The atomic weight is that quantity of an element which at any given temperature contains the same amount of heat as 7 parts by weight of lithium* (see p. 32).

Rule 1 is of course absolute, for, as the atom is regarded as indivisible, no fraction of an atom can be contained in any molecule. Thus, the molecular weight of hydrochloric acid, as determined by our general law (p. 59), is 36·5, and analysis shows this to be composed of 1 part by weight of hydrogen, and 35·5 parts by weight of chlorine (see also p. 69). Now, we are not acquainted with any compound which contains in its molecule less than this proportion of chlorine, and hence we take 35·5 as the atomic weight of chlorine.

The molecular weight of mercuric bichloride is 271, and analysis shows that in this substance 200 parts by weight of mercury, are combined with 71 parts by weight of chlorine; and, as no compound is known in the molecule of which there are less than 200 parts of mercury by weight, this number is taken as the atomic weight of mercury.

Again, the molecular weight of phosphoretted hydrogen is 34, and in this gas 31 parts by weight of phosphorus are united with 3 parts by weight of hydrogen; and, since no smaller proportion than 31 of phosphorus is known to exist in any molecule, this number is taken as the atomic weight.

In the case of all elements, the molecules of which consist, like the molecule of hydrogen, of 2 atoms, the specific gravity of their gas or vapour, compared to hydrogen, gives their atomic weight direct; but this relation does not hold good in the case of those elements, the molecule of which does not consist of two atoms. Taking our above three examples, it will be found that the specific gravity of the three elements—chlorine, mercury, and phosphorus, compared with hydrogen, are respectively 35·5, 100 and 62, whereas their atomic weights are 35·5, 200 and 31 respectively. Hence, the molecule of chlorine consists of two atoms, that of mercury contains one atom, that of phosphorus four. These atomic weights are also in harmony with all chemical facts known regarding these elements.

It will thus be seen that the atomic weight of an element may be determined without the necessity of volatilising the element itself; nor need the element be volatile, since its atomic weight can be calculated from the molecular weight of a volatile compound. Unless, however, we have some good reason to conclude that the molecule experimented on contains the smallest possible quantity of the element, the atomic weight of which has to be determined, something more than the mere knowledge of the molecular weight and percentage composition of the compound is necessary to fix the atomic weight of the element, and in such a case rule 2 often comes in. The specific heat of an element may, in fact, be taken as a valuable guide in fixing its atomic weight, but, owing to its liability to variation, can only be used as indicating approximately what particular simple multiple of a number accurately fixed by other means should be taken as the true one.

Thus, the specific gravity of the vapour of ferric chloride is 162·5 ($H = 1$); hence, its molecular weight is 325, and analysis shows that this compound contains 213 parts by weight of chlorine (6 atoms) to 112 parts by weight of iron. This latter weight we might take as the atomic weight of iron, were it not for the fact that the specific heat points to 56 as the true atomic weight, and this being in harmony with the chemical relations of iron is taken as such. The molecule of ferric chloride, therefore, contains two atoms of iron, and is not a compound containing the smallest possible quantity of iron in its molecule.

In many cases the accurate analysis of any compound coupled with a knowledge of the specific heat of the element, the atomic weight of which has to be determined, is sufficient to fix the value of the atomic weight apart from the necessity of volatilization (although this method should always be resorted to where possible). Thus, analysis of calcium chloride shows it to be a compound, in which the proportion by weight of chlorine to calcium is as 35·5 to 20. Now the specific heat of calcium is 0·1670, from which the atomic weight would be calculated as 37·7;* and this figure is sufficiently near to 20×2 as to leave no doubt on the mind, that the correct atomic weight of calcium is 40, and that the molecule of chloride of calcium consists of one atom of calcium united with two atoms of chlorine.

Occasionally, also, chemical analogy may guide us in determining a doubtful atomic weight, and isomorphism (p. 18) may not unfrequently assist us in the same object. The quantities which replace one another in isomorphous compounds, are also the relative atomic weights; and, if

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* The specific heat divided into 6·3 (the mean atomic heat of the solid elements).

we know the atomic weight of one element in such an isomorphous series, the atomic weights of all the others become known.

Lastly, we may define the terms atom and molecule as follows:—

1. An **atom** is the smallest portion of an element which can exist in the molecule of any one of its compounds.

2. A **molecule** is the smallest portion of an element or compound which is capable of independent existence.

Valency*[*] of the Elements.—A careful study of chemical compounds has shown that the various atoms of different elements are by no means equivalent to each other—they cannot each and all replace one another in compounds, in exact atomic proportions, that is, atom for atom. Thus, whereas, 23 parts by weight of sodium (1 atom) unite with 35·5 chlorine (1 atom) to form chloride of sodium, it is found that 40 parts by weight of calcium (also 1 atom) unite with 71 parts by weight of chlorine (2 atoms), and that 210 parts of bismuth (1 atom) unite with 106·5 parts by weight of chlorine (3 atoms). Or, again, we find the following combinations by weight—35·5 chlorine with 1 hydrogen, 16 oxygen with 2 hydrogen, 14 nitrogen with 3 hydrogen, 12 carbon with 4 hydrogen, and so on.

Or, in other words, in order to replace 1 atom of bismuth, calcium or sodium would require 3, 2, and 1 atoms of hydrogen or chlorine respectively, &c., &c.

This relative atom-replacing or combining power, or equivalence of the elements, has been variously termed their quantivalence, valency, or atomicity. Of these terms the second for many reasons is to be preferred. Elements which replace, or combine with, 1 atom of hydrogen or chlorine are called univalent, and those which replace or combine with 2, 3, 4, 5, 6, 7, and 8 hydrogen atoms are termed bi-, tri-, quadri-, quinqui-, sex-, septe-, and octo-valent; or monads, dyads, triads, tetrads, pentads, hexads, heptads, and octads respectively. Elements of even valency are termed *artiads*[†] those of uneven valency *perissads*.[‡]

Sometimes an element varies in its valency, but almost always by differences of 2, and in such cases the highest valency is assigned to the element. The sum of the valencies in any molecule is always an even number. The table on p. 81 shows the elements arranged according to their valency, while that on p. 65 gives in the alphabetical list the valency of each element.

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[*] Also called atomicity, quantivalence or dynamicity.

[†] *ἄρτιος, even.*

[‡] *περισσὸς, uneven.*

Table of Symbols, Atomic Weights, and Valencies of the Elements.*

NAME OF ELEMENT.	Atomic Symbol and Valency.	Atomic Weight.	NAME OF ELEMENT.	Atomic Symbol and Valency.	Atomic Weight.
Aluminium, .	Al^{iii}	27·1	Molybdenum,	Mo^{v}	95·9
Antimony, .	Sb^{v}	120·3	Nickel, . . .	Ni^{viii}	59
Arsenic, . .	As^{v}	75	Niobium, . .	Nb^{v}	94·2
Barium, . .	Ba^{ii}	137	Nitrogen, . .	N^{v}	14·041
Beryllium, .	Be^{ii}	9·1	Norwegium, .	Ng^{vi}	214
Bismuth, . .	Bi^{v}	208·0	Osmium, . .	Os^{viii}	192
Boron, . . .	B^{iii}	11·01	Oxygen, . .	O^{vi}	16
Bromine, . .	Br^{vii}	79·963	Palladium, .	Pd^{viii}	106
Cadmium, . .	Cd^{ii}	112·1	Phosphorus, .	P^{v}	31·03
Caesium, . .	Cs^{i}	132·9	Platinum, . .	Pt^{viii}	194·8
Calcium, . .	Ca^{ii}	40	Potassium, .	K^{i}	39·17
Carbon, . .	C^{iv}	12	Rhodium, . .	Rh^{viii}	103
Cerium, . .	Ce^{iii}	140·2	Rubidium, .	Rb^{i}	85·4
Chlorine, . .	Cl^{vii}	35·453	Ruthenium, .	Ru^{viii}	103·8
Chromium, .	Cr^{vi}	52·2	Samarium, .	Sm^{vii}	150
Cobalt, . . .	Co^{viii}	59	Scandium, .	Sc^{iii}	44·1
Copper, . .	Cu^{ii}	63·3	Selenium, . .	Se^{vi}	79·1
Decipium, . .	Dp^{iii}	159	Silver, . . .	Ag^{i}	107·938
Didymium, .	D^{iii}	144·75	Silicon, . . .	Si^{iv}	28·4
Erbium, . .	E^{ii}	166	Sodium, . .	Na^{i}	23·06
Fluorine, . .	F^{vii}	19	Strontium, .	Sr^{ii}	87·5
Gallium, . .	Ga^{iii}	69·9	Sulphur, . .	S^{vi}	32·06
Germanium, .	Ge	72·3	Tantalum, . .	Ta^{v}	183
Gold, . . .	Au^{iii}	197·2	Tellurium, .	Te^{vi}	125
Hydrogen, .	H^{i}	1	Thallium, . .	Tl^{iii}	204·1
Indium, . .	In^{iii}	113·7	Thorium, . .	Th^{iv}	232·4
Iodine, . . .	I^{vii}	126·86	Tin, ...	Sn^{iv}	118·1
Iridium, . .	Ir^{iv}	193·2	Titanium, . .	Ti^{iv}	48·1
Iron, . . .	Fe^{viii}	56	Tungsten, . .	W^{vi}	184
Lanthanum, .	La^{iii}	138·5	Uranium, . .	U^{vi}	239·4
Lead, . . .	Pb^{iv}	206·91	Vanadium, .	V^{v}	51·2
Lithium, . .	Li^{i}	7·03	Ytterbium, .	Yb^{iii}	173·2
Magnesium, .	Mg^{ii}	24·38	Yttrium, . .	Y^{ii}	88·7
Manganese, .	Mn^{vii}	55	Zinc, . . .	Zn^{ii}	65·5
Mercury, . .	Hg^{ii}	200·4	Zirconium, .	Zr^{vi}	90·7

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* The above atomic weights are from the most recent authorities, but we have not thought it necessary to alter the figures given in the text which are frequently whole numbers or more commonly used.

Molecular Combinations.—When two saturated compounds, *i.e.*, compounds in which all atomicities are active, combine with each other, the resulting compound is said to be a molecular combination. Water of crystallisation, for example, is in molecular combination with the salt. The combination might be explained on the assumption that atomicities, which, even in ordinary so-called saturated compounds, had remained latent, have become active, or in other words, by raising the assumed maximum atomicity of the elements involved. Inasmuch, however, as all such compounds seem to be less stable than ordinary atomic compounds, it is assumed that they are not due to ordinary affinity between atoms, but are combinations of molecules.

Specific Volume.—As the volume occupied by a free atom or molecule, in the gaseous condition, is in all cases the same, namely, 2 volumes (the molecule of hydrogen being taken as occupying 2 volumes, see page 60), substances in that condition possess, strictly speaking, no specific volume. We shall, therefore, use this term only in relation to the volume occupied by a weight of substance, in the liquid or solid condition, proportional to its atomic or molecular weight either free or when in combination.

Much difficulty has been experienced in selecting the conditions most favourable for comparison, since the specific gravity, and hence, also, the specific volume, of a solid or liquid, varies with the temperature, and in the case of a solid also, with its physical condition, whether amorphous or crystalline, &c., &c. It has, however, been found by Kopp, who has specially investigated the subject, that, when the specific gravity is taken at the boiling point for liquids, and at the melting point for solids, the most concordant results are obtained. *If then* m *is the atomic or molecular weight of any element or compound, and* d *its specific gravity at the desired temperature, then* $\frac{m}{d}$ = *specific volume.*

Much work will yet have to be done before the subject of specific volume can be thoroughly understood; but certain regularities have already been observed, some of which may be briefly mentioned here.

(*a.*) The specific volume of isomorphous elements in the free state is often, approximately, the same.

Name of Element.	Atomic Weight.	Specific Gravity.	Specific Volume.
Cl	35·5	1·38	25·2
Br	80	2·97	26·9
I	127	4·95	25·6
S	32	2·045	15·6
Se	79·4	4·8	16·6
Fe	56	7·8	7·2
Co	59	8·51	7
Ni	59	8·82	6·8
Mn	55	8·01	6·8

(*b.*) The specific volume of an element in combination is not always the same as it is in the free state. Thus—

Name of Element.	Specific Volume when Free.	Specific Volume in Combination.
Cl	25·2	22·8
Br	26·9	27·8
S	25·6	37·5
K	45·5	30·2 in K_2O.
Na	23·7	15·9 in Na_2O.

(*c.*) The specific volume of an element has also frequently a different value in different compounds. Thus, on the assumption that the specific volume of a compound is the sum of the specific volumes of its constituents, the specific volumes of the constituents can be calculated from a number of simple compounds, and the following values are thus obtained, at least in the case of liquid compounds:—

Element.	Atomic Volume.
C	11
H	5·5
Cl	22·8
Br	27·8
I	37·5
O	12·2 when both affinities are saturated by a single atom.
O	7·8 when both affinities are saturated by two atoms.
S	28·6 when combined with a single atom.
S	22·6 when joining two atoms.
N	2·3 when united to three atoms.
N	17 when united to only 1 atom ($C=11$).
N	8·6 in the group NO_2 ($O=12·2$).

By means of these values the specific volumes of a great many compounds may be calculated with a fair degree of accuracy. Thus—

Substance.	Formula.	Specific Volume.	
		Calculated.	Found.
Benzol, ...	$C_6 H_6$	99	96 to 99·7
Water, ...	$H_2 O$	18·8	18·8
Acetic Acid, . . .	$C_2 H_4 O_2$	64	63·5 to 63·8
Chloroform, . . .	$C H Cl_3$	84·9	84·8 to 85·7
Nitric Peroxide, . .	$(NO_2)_2$	33	31·7 to 32·4

(*d.*) The specific volume of isomeric substances ought, on the above assumption, to be the same, and this is found to be the case; thus—

Acetic acid, $H, C_2 H_3 O$, has a specific volume of 63·5 to 63·8, while methylic formiate, $C H_3 C H O_2$, has a specific volume of 63·4.

(*e.*) In the case of solid substances the specific volume shows less regularities than in the case of liquids, but even here certain relations have been recognised.

Thus, isomorphous substances have the same specific volume (approximately).

Substance.	Molecular Weight.	Specific Gravity.	Specific Volume.
ALUMS.			
$(SO_4)_2\,Al\,K, 12\,H_2\,O$,	474·6	1·722	275·6
$(SO_4)_2\,Cr\,N\,H_4, 12\,H_2\,O$,	478·4	1·736	278·6
$(SO_4)_2\,Cr\,K, 12\,H_2\,O$,	499·5	1·845	270·7
$(SO_4)_2\,Fe\,N\,H_4, 12\,H_2\,O$,	482	1·712	281·5
SULPHATES.			
$SO_4\,Mg, 7\,H_2\,O$,	246	1·685	146
$SO_4\,Zn, 7\,H_2\,O$,	287	1·953	147
$SO_4\,Ni, 7\,H_2\,O$,	281	1·931	148·5
$SO_4\,Fe, 7\,H_2\,O$,	278	1·884	147·6

Here also, as in the case of liquids, the specific volume of an element may vary in different compounds.

Thus, in some oxides, as, for example, in plumbic and cupric oxides, the specific volume of oxygen, calculated on the assumption that the specific volume of the metal in the compound is the same as it was in the free state, is respectively 5·6 and 5·2; whereas in some other oxides, on the same assumption regarding the metal, the specific volume of the oxygen has at least three different values.

There are very notable exceptions to this law, however. Thus sodium chloride ($NaCl$) and potassium chloride ($K\,Cl$) are isomorphous, but their specific volumes are 27·2 and 38·7 respectively.

CHAPTER XI.

CHEMICAL NOTATION.

Symbols and Formulæ.—The symbols of the elements form the basis of chemical notation. Every element is represented by a symbol, which is in all cases the first letter of the Latin name of the element; to this is added, if necessary, the second or some other letter of the name, in order to distinguish between different elements, the names of which begin with the same letter—*e.g.*, C, Ca, Ce, Cu, for carbon, calcium, cerium, copper.

The symbol of an element, however, does not stand merely for an abbreviation of the name, but also for an atomic proportion of that element. Thus, the symbols H, O, N, Cl, K, Ca, mean respectively, 1 part by weight of hydrogen, 16 of oxygen, 14 of nitrogen, 35·5 of chlorine, 39 of potassium, and 40 of calcium, and they imply all that is implied in the conception of an atom.

Elements, as we know, combine with one another in atomic proportions, and the compounds so formed are represented symbolically by writing the symbols of the combining elements side by side—*e.g.*,

Hydrochloric acid,	HCl	Potassic hydrate,	KHO
Calcium oxide,	CaO	Plumbic sulphide,	PbS

If the molecule of a compound contains more than one atom of a particular element, this is indicated by a number placed to the right of the elementary symbol—*e.g.*,

Calcic carbonate,	$CaCO_3$	Ferrous sulphate,	$FeSO_4$
Manganese dioxide,	MnO_2	Sulphurous acid,	$H_2S_2O_3$.

If more than one molecule of a compound is to be notified, this is done by placing a number to the left of the symbol, and on a level with it—*e.g.*,

$$2\,HCl;\ 3\,KHO;\ 3\,CaCl_2;\ 4\,H_2O.$$

These *formulæ*, as they are called, are based, in the first instance, upon quantitative analysis, the results of which it is usual to express in percentages. From these percentages the atomic proportions may be calculated and the formulæ constructed.

For example, in hydrochloric acid, we find 2·74 per cent. hydrogen, and 97·26 per cent. chlorine, or 1 hydrogen to 35·49 chlorine. The specific gravity of hydrochloric acid is 18·25 ($H = 1$); hence, its molecular weight = 36·5 (p. 62), and the formula HCl, on the above assumptions, represents all these facts.

As already stated (p. 63) the molecular weight of a compound can sometimes be only indirectly determined, but the atomic weights of the constituent elements being known, the formula may be constructed from the percentage composition and from chemical analogy. Thus, black oxide of manganese has the percentage composition—manganese, 63·22 per cent.; oxygen, 36·78 per cent. Taking the atomic weights of these two elements as 55 and 16 respectively, we have the proportions—

$$55 : 63{\cdot}22 :: 1 : 1{\cdot}14$$
$$16 : 36{\cdot}78 :: 1 : 2{\cdot}29.$$

As the figures, 1·14 and 2·29, stand in the proportion of 1 : 2, we conclude that in the molecule of the oxide there are, at least, 1 atom of manganese and 2 of oxygen, and write its formula, MnO_2.

The percentage composition of marble is—calcium, 40 per cent.; carbon, 12 per cent.; oxygen, 48 per cent., by the same process as in the previous example; or, which comes to the same thing, by dividing these percentages by the atomic weights of their respective elements, we get 1 : 1 : 3, and write its formula, $CaCO_3$.

The valency of an element (p. 64) may be indicated by dashes or Roman numerals placed on the right to the top of the symbol, as H' (monad), O'' (dyad), B''' (triad), C'''' or C^{iv} (tetrad). Elements, as already stated, are not of the same valency in all their compounds, but the variation almost always takes place by twos, and the maximum valency can always be called forth. This variation can be indicated by representing the valencies active in the compound by dashes to the right, and those which are inactive or "latent" by dashes to the left—*e.g.*,

$${}^{\prime\prime}N^{\prime\prime\prime}H_3;\ {}^{iv}N_2O^{\prime\prime};\ N^{v}H^{\prime}_4Cl^{\prime}.$$

Chemical Equations.—Reactions taking place between compounds or elements are represented by equations; the compounds or elements as they exist before the change are placed on the left, those which exist after the change being placed on the right. In either case the compounds are separated by + signs—*e.g.*,

$$K_2 + 2\,H_2O = 2\,KHO + H_2$$

$$3\,MnO_2 = Mn_3O_4 + O_2$$

$$P_2 + O_5 = P_2O_5.$$

The equality implied extends only to the number of elementary atoms and their respective weights, and, consequently, to the weight of the substances before and after the reaction, but in no other sense is there equality.

The − sign is used in equations in its ordinary sense, denoting subtraction—*e.g.*,

$$PH_3O_4 - H_2O = PHO_3.$$

Brackets are sometimes used to enable us to indicate readily a multiplicity of molecules of any particular compound taking part in a reaction, sometimes also for expressing chemical combinations between elements or groups of elements placed vertically under each other—*e.g.*,

$$3\,(CaP_2O_6) + C_{10} = Ca_3P_2O_8 + P_4 + 10\,CO;$$

$$\left\{\begin{array}{l} NO_2O \\ Ba \\ NO_2O. \end{array}\right.$$

Empirical and Rational Formulæ.—The ordinary chemical formulæ, such as those with which we have been dealing, are called *empirical* formulæ*, and express a variety of information. They tell us—(*a.*) The elements contained in the compound; (*b.*) the proportion by weight and by volume in which they are combined; (*c.*) the number of atoms in the molecule; (*d.*) the molecular weight of the compound. But, formulæ may be constructed so as to represent with more or less

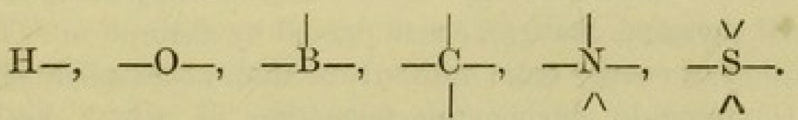
* ἐμπειρικὸς, *experimental.*

correctness the manner in which the various atoms are united within the molecule, or to indicate certain possible reactions or decompositions of the molecule of a compound, when acted upon by other compounds or by certain forces. For example, the empirical formula of sulphuric acid is H_2SO_4, but we may construct formulæ to indicate various facts relating to this compound. Thus, the formula SO_3, H_2O indicates that it may be broken up into sulphuric anhydride and water, or the formula SO_2, $2\,HO$ represents the assumption, that the molecule of sulphuric acid contains two molecules of hydroxyl, and so on. These last-mentioned formulæ are called *rational.*[*]

The empirical formula of crystallised sulphate of magnesium is $MgSO_{11}H_{14}$. If this substance is heated to 150°, it loses six molecules of water; to expel the seventh a higher temperature is required. These facts may be indicated, as well as some of the other points connected with sulphuric acid, by the formulæ—

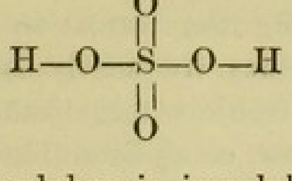
$$MgSO_4,\ 7\,H_2O, \text{ or } SO_2,\ MgO_2,\ H_2O,\ 6\,\text{aq.}$$[†]

Sometimes the constitution of a compound may be most clearly expressed by indicating the valencies of the various elements, and the manner in which these are disposed in the compound. This may be done, either as beforesaid, by dashes, or lines, sometimes called *bonds*, may be attached to the symbol; thus,



$$H-,\quad -O-,\quad -\overset{|}{B}-,\quad -\underset{|}{\overset{|}{C}}-,\quad -\underset{\wedge}{\overset{|}{N}}-,\quad -\underset{\wedge}{\overset{\vee}{S}}-.$$

Sulphuric acid may then be represented—thus



$$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$$

indicating that the hexad sulphur is, in sulphuric acid, united directly to the four atoms of dyad oxygen, to two of these with two bonds, to two with one bond only, the latter two oxygen atoms being each in their turn, united with their remaining bond to one atom of monad hydrogen.

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[*] Ratio, *a system.*

[†] Aqua, *water.*

CHAPTER XII.

THERMO-CHEMISTRY.

THE subject of thermo-chemistry has, of late years, assumed great importance. In alluding to it here, we must, however, confine ourselves to its more prominent features only, and must refer the student, who is anxious to pursue the subject in detail, to the celebrated works of Berthelot, Thomsen, Naumann, and others.

All chemical changes are associated with changes of temperature. These changes of temperature may either be *positive* (exothermic,[*] producing heat), or *negative* (endothermic,[†] absorbing heat); but, whether positive or negative, the amount of heat produced or absorbed is an invariable quantity for any given combination, though varying very considerably in different combinations. The principal conclusions arrived at may be shortly formulated as follows:—

(*a.*) The amount of heat evolved or absorbed during the formation of any given compound, will be absorbed or evolved when the compound is again decomposed.

(*b.*) All chemical changes, which, when once started, proceed without the aid of external energy, are accompanied by evolution of heat.

(*c.*) All chemical changes, accompanied by absorption of heat, require the addition of energy from without for their accomplishment.

(*d.*) Compounds, during the formation of which heat has been evolved, do not decompose spontaneously, and are, generally speaking, the more stable the greater the amount of heat evolved.

(*e.*) Compounds, during the formation of which, heat has been absorbed, are unstable; they frequently decompose spontaneously, or are decomposed by even feeble external causes, such as a slight elevation of temperature, a blow, catalytic action (p. 54), &c.

(*f.*) The quantity of heat evolved in a reaction is a measure of the sum of the physical and chemical changes which occur in this reaction.

(*g.*) The total thermal value of any reaction is dependent only on the initial and final stages of the changing system. This, like other laws of thermo-chemistry, is simply a consequence of the conservation of energy. It enables us to calculate the heat of formation of a compound which cannot be estimated directly, if only we can assume it as a link in a series of reactions, all the other heat factors of which are

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ἔξω, *without, out of*; θέρμη, *heat*.

[†] ἔνδον, *within*; θέρμη, *heat*.

known. Thus, the molecule* of formic acid ($C H_2 O_2$), when burnt in oxygen, yields carbonic anhydride (CO_2) and water (H_2O), and evolves 65,900 calorics or units of heat (p. 31) in the process; and, if we burn the same amount of carbon and hydrogen contained in this molecule of formic acid directly to carbon dioxide and water, the heat evolved amounts to 165,320 units. Now, according to our law, the same amount of heat will be evolved if we first united these elements into formic acid, and then converted this into carbon dioxide and water, as if we burnt the carbon and hydrogen directly into these compounds; hence, it follows that the heat formation of formic acid must be 165,320 − 65,900 = 99,420 units.

(*h.*) Every chemical change accomplished without the addition of external energy tends to the formation of that body or system of bodies, the production of which is accompanied by the evolution of the maximum quantity of heat. This law is usually known as Berthelot's law of maximum work, but, although true generally, does not seem to be so universally.

This law of maximum work is one of considerable importance. It will often enable us to decide beforehand whether a contemplated reaction is or is not possible by direct means, and if, because accompanied by absorption of heat, not possible in the direct way, it may enable us to bring it about by making it one of a series of reactions, the total effect of which is an evolution of heat.

The combination of silver with chlorine and with iodine respectively, is accompanied with the evolution of 29,380 and 13,800 units of heat; and, accordingly, we find that chlorine ejects iodine from its combination with silver. On the other hand, hydrochloric and hydriodic acids, in acting upon oxide of silver, evolve respectively 38,610 and 51,070 units of heat; in accordance with which we find that hydriodic acid ejects chlorine from its combination with silver, with the formation of iodide of silver and hydrochloric acid. The reversal of the action is explained by the difference in the heat evolved; in both cases, that compound is formed in the formation of which the greatest amount of heat is evolved.

The presence or absence of a solvent has often considerable influence on the amount of heat evolved in a reaction, and in consequence has frequently a considerable influence on the ultimate result of a reaction.

The production of peroxide of hydrogen from water is accompanied by absorption of heat, and cannot, therefore, be accomplished by

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* All molecular or atomic quantities alluded to in this chapter must be considered as expressed in grammes.

chemical means alone in the direct way; but we can effect it by making it depend on the simultaneous formation of chloride of barium from binoxide of barium, a reaction in which more heat is evolved than is absorbed in the formation of peroxide of hydrogen from water.

The law of maximum work apparently does not hold good in the case of combinations between acids and bases in aqueous solution, for, according to Thomson, if to two bases only enough acid is added to unite with or neutralise one, the greater part of the acid frequently unites with that base with which it produces least heat.

CHAPTER XIII.

CHEMICAL AFFINITY.

By *chemical affinity* is understood that force under the influence of which substances combine with one another to form new compounds, differing permanently in their properties from those of their constituents.

Differences between a Mechanical Mixture and a Chemical Compound.—It is important to the beginner to be clear on the point that a chemical compound is something very different from a mere mechanical mixture. The following statement includes the more prominent differences between them:—

1. The properties of a mechanical mixture are the mean of those of its constituents; whereas, in a chemical compound (with very few exceptions), they are widely different from them. 2. The relative quantities of the constituent elements of a mechanical mixture may be varied, while those of a chemical compound are fixed and unalterable. 3. From a mechanical mixture the constituents can be separated by mechanical means, while in a chemical compound this is not possible. 4. During the formation of a mechanical mixture no alteration of temperature necessarily occurs, while this is always the case in the formation of a chemical compound.

The term "affinity" has not been happily chosen, for, so far from indicating any close relationship, this force of atttraction is strongest between substances most widely different from each other. The exact nature of the force called chemical affinity is not known, but as a force of attraction it differs from other similar forces in various ways. Thus, it differs from gravitation, inasmuch as it only acts when substances are in intimate contact; whereas, gravitation acts at all distances; and from cohesion, by acting mainly between dissimilar substances.

The strength of this affinity varies greatly; it is strong between some substances, feeble between others, and even varies in strength between the same substances. Thus, steam (H_2O) passed over iron (Fe) heated to redness yields hydrogen (H_2), and produces oxide of iron ($Fe_3 O_4$); while hydrogen passed over heated oxide of iron produces steam and metallic iron. Or, again, oxide of calcium ($Ca O$) acting on a dilute solution of carbonate of soda ($Na_2 CO_3$), produces caustic soda ($Na HO$)

and carbonate of calcium (Ca CO_3), whereas, in a strong solution, this reaction is reversed. In these cases an alteration of the conditions has been sufficient to reverse the relative strength of the affinities.

Much also depends on the nature of the substances produced during a reaction; and, as a rule, if in a mixture of substances, a compound can be produced which is either insoluble or gaseous under the conditions of the experiment, this compound will be formed. Thus, in an aqueous solution, the addition of acetic acid ($C_2 H_4 O_2$) to carbonate of soda ($Na_2 CO_3$) yields acetate of soda ($Na C_2 H_3 O_2$) and carbonic acid (CO_2); whereas, the passing of carbonic acid into an alcoholic solution of acetate of sodium yields carbonate of soda, which is precipitated (being insoluble in alcohol), and acetic acid. In aqueous solution boric acid is expelled from its salts by almost every acid, whereas, it drives out the strongest volatile acids from their salts, if it can be heated with these salts to redness.

Comparatively slight variations of temperature also frequently bring about variations in the force of chemical affinity. Thus, mercury heated in contact with air for some time near its boiling point, unites with the oxygen and forms oxide of mercury, while this oxide of mercury, when heated to a somewhat higher temperature, breaks up into metallic mercury and oxygen.

When in a mixture of salts* in solution, no insoluble salt is produced, all possible salts will probably be formed, that is, every acid present will combine with every base, but the relative quantity of any one of the salts formed, compared to the total quantity which might be formed if no other acids or bases were present, is not known. This quantity does not however seem to be governed, in all cases, in accordance with the amount of heat which might be evolved. In solution the amount of any particular salt or compound formed seems, however, to increase regularly with the increase of the particular substance added. In the case of gases this is not, however, the case. According to Bunsen, for example, the quantities of carbonic acid and water, formed when mixtures of carbonic oxide and hydrogen are exploded, with an insufficient amount of oxygen, always stand to one another in some simple atomic relation. This relation remains the same within certain limits of variation in the proportions of the gases exploded, and does not alter proportionally to the alteration in quantity of one or other of the constituents. When, however, certain limits are overstepped, the proportion changes suddenly from one atomic proportion to some other, which is, however, also an atomic proportion.

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* *Vide* oxygen.

Many of the foregoing alterations or reversals of the strength of chemical affinities between given sets of substances, find their explanation in corresponding variations in the heat relations of the compounds formed. The variation in the strength of chemical affinity between elements and compounds, and the possibility of their reversal under certain conditions are among the most powerful means which the chemist possesses for producing chemical changes. (See *note*, p. 78.)

Dissociation.—The term dissociation was first used to explain certain apparently anomalous vapour densities. Thus, the accepted molecules of chloride of ammonium (NH_4Cl), and of sulphuric acid (H_2SO_4) were found to occupy 4 instead of the normal 2 volumes (p. 60). Now the formulæ of these molecules could not be altered so as to halve the molecular weight, and so make the molecule occupy only 2 volumes, but some other explanation of the facts observed became necessary. This was found in the assumption, for which there is, however, some experimental evidence, that these two substances, when heated, break up into two molecules, each occupying its normal 2 volumes, and together, therefore, 4 volumes. NH_4Cl and H_2SO_4 break up respectively into NH_3, HCl and SO_3, H_2O. On cooling, these constituents reunite, and produce the original compound. The decomposition thus assumed to take place in the gaseous form of these substances at a higher temperature was termed *dissociation*. The term has now, however, been extended to all decompositions produced by heat in which, during cooling, reunion of the separated constituents takes place.

If the substance is heated in a closed vessel so that the dissociated product or products, some of which must be gaseous, cannot escape, they will exert a certain pressure, and, under these circumstances, it is found that the tension of the products is definite for any given temperature, and is independent of the amount of substance present. If the temperature is raised dissociation increases, if it falls partial reunion takes place. Both high temperature and low tension favour dissociation, low temperature and high tension favour union.*

These phenomena of dissociation are closely related to those of evaporation, in both a similar correlation between temperature and tension exists.

It will be easily understood that the temperature produced by the union

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* If, for example, a relatively small amount of calcium carbonate is put into a vessel and heated, almost the whole of the compound may become dissociated before the necessary tension of the carbonic anhydride due to the temperature is reached; if, on the other hand, a relatively large amount of calcium carbonate is put into the same vessel, a very small part of it only will be decomposed at the same temperature, though the actual amount of substance decomposed is the same in both cases.

of two or more substances can never rise to that point at which complete dissociation of the products of such union would take place. Supposing the substances to have been heated to that temperature, union can only begin when the temperature has fallen below that of dissociation.

Electrolysis.—The decomposition of chemical compounds effected by an electric current is termed *electrolysis*.[*] The substance decomposed is called the *electrolyte*,[†] the parts into which it is decomposed are called *ions*,[‡] and the parts of the circuit at which the ions make their appearance, namely, those parts at which the current enters and leaves the electrolyte, are called *electrodes*.[§] One electrode, the one connected with the electro-positive plate of the battery, that is, the plate acted on, is negative, and at it such substances as hydrogen, metals, and alkalies make their appearance, which are, therefore, called electro-positive: the other electrode, the one connected with the negative plate of the battery, is positive, and at it substances like chlorine, bromine, oxygen, and acids make their appearance, and are called in consequence electro-negative. Hence, the division of elements into electro-positive and electro-negative respectively.

An electrolyte must be a liquid, and is generally composed of a conductor and a non-conductor.

The amount of decomposition effected in an electrolyte is always proportional to the quantity of electricity passing through it.

The same quantity of electricity decomposes equivalent quantities of various electrolytes, or liberates equivalent quantities of the various elements or compounds.

The laws given in the last two paragraphs were first established by Faraday, and are known as Faraday's Electrolytic Law, the second part of which may be stated in the language of modern chemistry, thus:—The same electric current is able to overcome the same number of active atomicities, whatever the electrolyte may be; or the various quantities of elements liberated are proportional to their atomic weights, divided by their active atomicities. Thus, an electric current which would liberate 1 part of hydrogen would liberate 35·5 of chlorine, (1 atom); 80 bromine (1 atom); 108 silver (1 atom); 103·75 lead ($\frac{1}{2}$ atomic proportion); 8 oxygen ($\frac{1}{2}$ atomic proportion), &c. In the case of elements of varying atomicity, the proportion of the element liberated, or of compound decomposed, varies with the atomicities engaged. Thus a current which will decompose 134·2 parts cupric chloride ($Cu'' Cl_2$) will decompose 197·4 parts of cuprous chloride ($Cu'_2 Cl_2$).

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[*] λύσις, *separation.*

[†] λύω, *I set free.*

[‡] ἰών, *going.*

[§] ὁδός, *a way.*

Compound Radicals.—Elements are not only replaceable by elements, but also, not unfrequently, by certain compounds or groups of elements which in such cases play the part of a single element, and are then termed *compound radicals.* Such compound radicals, though chiefly occurring in organic compounds, are also met with in inorganic. Thus carbonic oxide (CO) frequently plays the part of a radical (called carbonyl) combining directly with elements, as, for example, in carbonyl chloride, $CO\,Cl_2$.

Other such compound radicals are—hydroxyl $(HO)_2$, ammonium $(NH_4)_2$, nitryl (NO_2), sulphuryl (SO_2), &c. These radicals, like the elements, differ in their valency or atom-combining power, being uni-, bi-, trivalent, &c., as the case may be. Like the elements also, compound radicals of uneven valency are unable to exist by themselves, but combine with one another to form compounds analogous to the molecules of elements, in which cases the radical itself, though strictly speaking a compound, is often termed an atom to indicate this analogy.

Substitution.—The replacement of one or more atoms in the molecule of a compound by one or more other atoms, elementary or compound (radicals), is known as *substitution.* The term substitution is, however, more frequently used to denote the replacement of one or more atoms or radicals in an organic compound without alteration of the general chemical characteristics of the original compound.

The mutual interchange between two compounds of part of their constituents is known as *double decomposition*, and is perhaps the most common of all chemical actions, as, for example, when a solution of potassium sulphate is added to a solution of barium chloride, the result being the formation of barium sulphate and potassium chloride, thus—

$$Ba\,Cl_2 + K_2\,SO_4 = Ba\,SO_4 + 2\,K\,Cl.$$

Even the direct union of elements may be considered as, in reality, a case of double decomposition, as when hydrogen unites with chlorine to form hydrochloric acid, thus—

$$H-H + Cl-Cl = H-Cl + H - Cl.$$

" *Note.* See p. 76.—In many cases the presence of a third substance appears to be necessary to enable two other substances to act chemically on each other; thus, pure zinc is far less readily dissolved by acids than impure zinc, and pure nitric acid dissolves many metals far less readily than when it contains some nitrous acid. Indeed, it appears that perfectly pure nitric acid has no action on copper, and that action only begins when a trace of nitrous acid is present. Again, it has been shown, that phosphorus does not burn in absolutely dry oxygen, and that a perfectly dry mixture of carbonic oxide and oxygen cannot be exploded by an electric spark.

CHAPTER XIV.

CLASSIFICATION OF ELEMENTS.

ELEMENTS have long been divided into two great classes—*metalloids*[*] (or, better, *non-metals*) and *metals*.[†] This division was based mainly, if not entirely, on physical characteristics. It was found later on that the division coincided broadly also with certain well-marked chemical characters, but these chemical characters should be considered as only of secondary importance in a classification based on physical peculiarities.[‡] Non-metals, as a class, are bad conductors of heat and electricity, and have no characteristic lustre in common; metals, on the other hand, are, as a class, good conductors of heat and electricity, and are characterised by a peculiar lustre by which they are readily recognised as metals, even by an unskilled observer: this lustre is termed *metallic* in default of any other standard of comparison. As a rule, the oxides formed by non-metals yield acids, and no well-marked basic oxide is formed by any of them. On the other hand, the metals form basic oxides mainly (*vide* oxygen).

The following elements are commonly regarded as non-metals. Of those included in brackets, hydrogen is now very generally regarded as a metal, and arsenic and antimony are only included by some among the non-metals, on account of their chemical relations to phosphorus.

Table of Non-Metals.

Oxygen,
Sulphur,
Selenium,
Tellurium,

(Hydrogen),
Chlorine,
Bromine,
Iodine,
Fluorine,

Nitrogen,
Phosphorus,
(Arsenic),
(Antimony),

Carbon,
Boron,
Silicon.

The rest of the elements come under the general heading of "metals."

According to other partial classifications the elements may be arranged in groups, frequently of three members, characterised by a certain uniformity in chemical properties, and showing certain grada-

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[*] *μέταλλον, a metal;* and *εἶδος, likeness.*

[†] *μέταλλον, a mine, metal.*

[‡] The term metalloid is extremely inappropriate, applied to the class of non-metals. Tilden suggests to include under the term metalloid a number of elements, whose properties are intermediate between those of non-metals and metals.

tions corresponding to certain relations between their atomic weights, such as the groups Cl, Br, I; Ba, Sr, Ca, &c. Again, elements may be classified according to their valency into monads, dyads, triads, &c., or into elements of even valency (artiads), and elements of uneven valency (perissads).

The most complete classification, however, as yet attempted, is that proposed by Mr. John A. R. Newlands under the name of the "Law of Octaves." Newlands showed that, if the elements are arranged in the order of their atomic weights (regarding elements with the same, or nearly the same atomic weight as one), there is a regular periodic recurrence of similar characteristics; that, in fact, the properties of the elements are a periodic function of their atomic weights. Broadly speaking, this reappearance of similar properties occurs in every eighth element, and, hence, the term "Law of Octaves." This periodicity, once recognised, leads to most important conclusions, as clearly pointed out by Newlands in his original papers.* Thus, accepted atomic weights may be corrected in cases in which the character of the element does not correspond with those indicated by its place in the series; the existence of unknown elements may be inferred from the occurrence of vacant places in the classification, and even the properties of unknown elements may be, in great measure, predicted.

Mendelejeff, who has most completely worked out this law, and calls it the "Periodic Law," arranges the elements in eight groups and twelve series, as shown in the table on next page.

The members of each group show similarity in their chemical and physical characters, more especially of the even and odd series respectively, as will readily be seen by an inspection of the table, in which the even series is printed in italic type. On the other hand, the members of one series show a regular gradation of properties, as we proceed from one member to the other. Thus, as we pass from group I. to group VII., we pass from electro-positive by slow gradations to electro-negative elements (p. 77), and from group I. to group VIII. there is a regular increase of one in the number of atoms of oxygen with which each element can combine, and we have, further, a regular alternation of perissad and artiad elements (p. 63). In series 2 and 3 we pass through all gradations, from positive to negative, in each series of seven members; in the other series, the cycle is only completed in two series or fourteen members, not counting group VIII. Mendelejeff calls the first two short periods, the other long periods. Group VIII. is some-

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* Lately published in a collected form, entitled *On the Discovery of the Periodic Law*, by J. A. R. Newlands, F.I.C., F.C.S., &c. Spon, London, 1884.

Table of Mendelejeff.

Series.	GROUP.									
	I. R_2O	II. R_2O_2	III. R_2O_3	IV. RH_4 R_2O_4	V. RH_3 R_2O_5	VI. RH_2 R_2O_6	VII. RH R_2O_7	VIII. (R_2H) (R_2O_8)		
1	H = 1									
2	*Li = 7*	*Be = 9*	*B = 11*	*C = 12*	*N = 14*	*O = 16*	*F = 19*			
3	Na = 23	Mg = 24	Al = 27·3	Si = 28	P = 31	S = 32	Cl = 35·5			
4	*K = 39*	*Ca = 40*	*Sc = 44*	*Ti = 48*	*V = 51·3*	*Cr = 52*	*Mn = 55*	*Fe = 56*	*Co = 58·6*	*Ni = 58·6*
5	Cu = 63·2	Zn = 65·3	Ga = 68·8	?	As = 75	Se = 79	Br = 80			
6	*Rb = 85·3*	*Sr = 87·5*	*Y = 89·8?*	*Zr = 90*	*Nb = 94*	*Mo = 95·5*	*100 ?*	*Ru = 104*	*Rh = 104*	**Pd = 105 7**
7	Ag = 107·7	Cd = 112	In = 113·4	Sn = 118	Sb = 120	Te = 125	I = 127			
8	*Cs = 133*	*Ba = 137*	*La = 138·5*	*Ce = 140·5*	*Di = 146*	*Tb? = 148·8*	*Sm? = 150*	*? 152*	*?*	*?*
9	?	?	Dp ? 159	?	Er ? 165·9	?	?			
10	*?*	*?*	*Yb = 172·8*	*?*	*Ta = 182*	*W = 184*	*?*	*Os 198·6 ?*	*Ir = 192·5*	*Pt = 194·4*
11	Au = 196	Hg = 200	Tl = 204	Pb = 206·5	Bi = 208·2	Ng ? 214	?			
12	*?*	*?*	*?*	*Th = 233·4*	*?*	*U = 238·5*	*?*			

what anomalous, as each member of the group is, so to speak, represented by three elements. Mendelejeff calls them transition elements, and places them between the even and odd series of the long periods. Further, the atomic volume (p. 63) changes periodically with the atomic weight, showing maxima and minima. Now, a comparison of the maxima of atomic volume with the above table, shows, wherever the comparison can be made, that these coincide with the first members of Mendelejeff's short and long periods—*e.g.*, Li, Na, K, Rb, Cs. This coincidence is all the more striking, because the periodic variation of atomic volume was worked out by Meyer independently of the periodic law of Mendelejeff. The places where a ? is placed in the table indicate the probable existence of unknown elements.

Many other relations might be pointed out, and will occur to every one who studies the table carefully, but enough has been said to demonstrate the truth of the law, that the properties of the elements are a periodic function of their atomic weights. At present, we do not know the cause of this periodicity, but, nevertheless, the discovery of the law by Newlands marks one of the most remarkable advances in the science of chemistry.

In conclusion of this Introduction, we append a Scheme of Properties of any given Element or Compound, which we believe will be of considerable service to the student of chemistry. On a careful examination, it will be seen to serve several purposes. In the first place, it forms the basis of the arrangement of facts relating to the elements and their compounds, as treated of in the following pages. It is, at the same time, a summary of the foregoing Introduction, in which these facts have been dealt with from a general point of view. It may also form a convenient *aide mémoire* since, if committed to memory, it will enable the student to recall the various properties of any given element or compound which, unless arranged on some definite plan, may so easily escape recollection.

SCHEME OF PROPERTIES, &c., OF ANY ELEMENT OR COMPOUND.

Name or *names* (*Derivation of Name*).

Symbol and **At. Wt.** (*if an Element*).

Formula, Mol. Wt., and **Percentage Composition** (*if a Compound*).

Occurrence in Nature (*if at all—abundant or rare—Distribution*).

PHYSICAL PROPERTIES.

State of Aggregation *at Ordinary Temperatures.*	If **Solid,** *Melting and Boiling Pt., Cryst. Form, if any.*
	If **Liquid,** *Freezing and Boiling Pt., Vapour Tension.*
	If **Gas,** *Temp. and Pressure for required Liq*$^{n.}$ *and Solid*$^{n.}$

Specific Gravity (*according to Physical Condition*).

Colour, Odour, Taste.

Solubility.

Behaviour to Heat (*Expansion, Conduction, Latent and Sp. Heat*).

" " **Light** (*Refraction, Transparency or Opacity, &c.*)

" " **Electricity** (*Conduction, Magnetic or Diamagnetic, &c.*)

CHEMICAL PROPERTIES.

IF AN ELEMENT.

Class or **Group** *of Elements to which it belongs.*

Chemical Behaviour *to other Elements and Compounds.*

Heat of Combustion.

Valency—Atomic Volume.

IF A COMPOUND.

Class or **Group** *of Compounds to which it belongs.*

Chemical Behaviour *to other Compounds or Elements.*

Analysis (*Decomposition*) and **Synthesis** (*Production*).

Heat of Formation.

Specific Volume.

Distinguishing Tests.

Physiological Action (*Application in Medicine*).

Preparation or **Manufacture.**

Applications (*in the Arts or in Common Life*).

Historical Matter.

OXYGEN.

(ὀξύς, *acid*, γεννάω, *I produce*) $O = 16$; $O_2 = 32$. *Gas at ordinary temperatures. Liquid at* −182° *under* 1 *atmosphere pressure, or at* −113° *under* 50 *atmospheres pressure* (*critical temperature and pressure*†). *Specific gravity of gas* 1·108 (*air* = 1); 16 ($H = 1$); *of liquid at* −182, 1·124 (*water* = 1). *Dyad.** 11·19 *litres weigh* 16 *grammes.*

Occurrence in Nature.—Oxygen is the most widely diffused and most abundant element in nature. It is variously estimated to constitute from $\frac{1}{3}$ to $\frac{1}{2}$ by weight of the earth's crust, as far as this is accessible to research. It forms $\frac{1}{5}$ of the bulk, and rather more by weight, of the earth's atmosphere, and $\frac{8}{9}$ by weight of water. It is found in combination in nearly every mineral and rock (the chief exceptions being rock-salt, fluor-spar, and pyrites), in all soils, and in almost all animal and vegetable matter. The following very brief list of common substances containing it, may serve to emphasise its diffusion and abundance :—

Percentage of Oxygen in some Common Substances.

Albumen (white of egg),	about 22·0	Cellulose (Woody Fibre),	about 49·3
Air,	23·0	Clay,	52·0
Iron Rust (Oxide of Iron),	40·0	Flint, Quartz, &c.,	53·3
Limestone,	48·0	Water,	89·9

Physical Properties.—Oxygen is a colourless, tasteless, and odourless gas, which, until quite recently, was considered to be "*permanent*," i.e., *incondensible*. A pressure of 3000 atmospheres had failed to liquefy it at ordinary temperatures. In 1877, however, Pictet and Cailletet simultaneously succeeded in liquefying it by the conjoint action of intense cold and pressure.

Oxygen follows Boyle's law for moderately high pressures, but departs from it at very high pressures. Thus, at a pressure of 1000 atmospheres, it is only reduced to $\frac{1}{595}$ of its volume, instead of to $\frac{1}{1000}$.

It is slightly soluble in water; 100 vols. water absorb 4·11 vols. at 0°, 2·99 vols. at 15°. Its *coeff. of absorption for water* is 2·025 times that of nitrogen (Bunsen): hence, air dissolved in water is richer in oxygen than ordinary air. 100 vols. alcohol dissolve 2·84 vols. between 0° and 24°. It is also soluble in molten silver and platinum.

Its *coeff. of expansion* is 0·003674 between 0° and 100°. Its sp. heat = 0·2175 *under constant pressure* (Regnault). Its refractive power is less than that of any known substance. Its *absolute index of refraction* = 1·000272. It is magnetic (Faraday).

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* Hexad, according to Mendelejeff (p. 81).

† By critical pressure is meant the pressure exerted by a gas at its critical temperature. (See *critical point*, p. 51).

Chemical Properties.—The most striking chemical characteristic of oxygen is its universal, and, generally, intense combining power. Fluorine is the only element with which it is not known to form a compound.

Thus, at ordinary temperatures it combines with moist iron, with copper when moistened with hydrochloric acid, with phosphorus, with the metals of the alkalies and alkaline earths, with alkaline pyrogallates, with an alkaline solution of indigo white, with nitric oxide, with moist ferrous and some analogous oxides, &c., the reaction in each case being accompanied by an elevation of temperature. At higher temperatures it combines with many more substances, often with intense heat and brilliant light effects, as, for example, with carbon, phosphorus, sulphur, zinc, iron, magnesium, &c.

Many of the above reactions are employed for the detection of oxygen, for its removal from mixtures, or on account of the heat and light evolved, and many of them—notably the burning of carbon, of sulphur, and of phosphorus in pure oxygen—form some of the most familiar and brilliant lecture experiments.

The compounds of oxygen are termed oxides. The term *oxidation* means an addition of oxygen to, the term *reduction*, a removal of oxygen from, any substance. Hence, the terms *oxidising-* and *reducing-agents*, which are applied to substances capable of bringing about oxidation or reduction respectively.

Distinguishing Tests.—Oxygen may be distinguished from all other substances as a colourless gas, which causes a glowing splint or taper to burst sharply into flame, which also forms red fumes with nitric oxide (p. 121), and when exploded with twice its volume of hydrogen, forms water only. These two last reactions distinguish it from nitrous oxide (p. 119).

Physiological Action.—*Respiration* is essentially a process of oxidation. The oxygen of the air, taken into the lungs, passes by diffusion through the membranes of the capillary vessels into the blood, where it combines with the hemoglobin, the red colouring-matter of the blood, displacing an equal or nearly equal volume of carbonic anhydride. In the course of circulation the oxygen combined with the hemoglobin, oxidises some of the constituents of the tissues, with the ultimate formation of water and carbonic anhydride, which latter, on the return of the blood into the lungs, is in its turn displaced by the oxygen of the inspired air, the carbonic anhydride so displaced being expelled in the air expired. The life of all the higher animals depends upon this interchange of oxygen for carbonic anhydride.

Oxygen, when breathed in the pure state at ordinary temperature and pressure, produces considerable stimulating effects; at low temperature it produces narcotism, and eventually death.

It has proved useful as an antidote in cases of poisoning by carbonic anhydride. Many disease-germs lose their virulence by exposure to the action of oxygen.

Preparation.—There are many methods of preparing this gas, most of them being based on the decomposition of one or other of its numerous compounds by heat, for, although present in large quantity, and in the free state, in atmospheric air, the nitrogen with which it is mixed cannot practically be removed, and to obtain it from this source indirect methods have to be resorted to.

1. *By heating mercuric oxide* in a glass retort or tube, and causing the gas given off to pass through a bulb-tube kept cool; the mercuric oxide breaks up into oxygen and mercury, both of which are gaseous at the temperature of decomposition; the mercury condensing in the bulb-tube, the oxygen only passes on and may be collected over water.

$$\underset{\text{Mercuric Oxide.}}{2HgO} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2}.$$

This mode of preparation has chiefly a historical interest, since it was the process used by Priestley, the discoverer of oxygen; but a further interest attaches to it from the fact that it was the germ, so to speak, of the so-called indirect methods of obtaining oxygen from the atmosphere, for mercury, when heated in contact with air to a temperature a little below its boiling point, slowly absorbs oxygen, and becomes converted into mercuric oxide, from which substance, at a higher temperature, the oxygen may be regained.

2. *By heating potassium chlorate.*—This is the most convenient, and, perhaps, the best method for obtaining oxygen for laboratory purposes. The crystals are introduced into a dry retort or Florence flask, which is connected by means of a perforated cork and suitably bent tubing with a pneumatic trough. On application of heat, the salt first crackles or *decrepitates*, melts, and then enters into apparent ebullition. As the evolution of gas proceeds, the salt becomes less fluid, and the temperature must be raised in order to obtain a further quantity of oxygen. At this stage of the process, the salt has a great tendency to froth, and the retort should therefore never be more than half filled.

The oxygen so obtained is very pure, especially if the heat has been carefully regulated, so as not to evolve it too rapidly. The gas is sometimes cloudy, owing to finely-divided particles of the salt being carried over.

The first stage of the process may be thus represented—

$$\underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{2KClO_3} = \underset{\substack{\text{Potassium}\\\text{Perchlorate.}}}{KClO_4} + \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{KCl} + \underset{\text{Oxygen.}}{O_2}$$

The second stage, during which a higher temperature is necessary, thus—

$$KClO_4 = KCl + 2O_2$$

The beginning and the end of the operation are, however, generally represented thus—

$$2KClO_3 = 2KCl + 3O_2$$

The temperature required to produce oxygen from the pure potassium chlorate is, however, so high, that few glass vessels will withstand it, and it is therefore advisable, where the extreme purity of the gas is no consideration, to mix the salt with one-eighth of its weight of previously ignited manganese dioxide (MnO_2). The oxygen is now given off much more readily, and at a very much lower temperature, the salt not even fusing; but the evolution of the gas may be very violent, and the temperature should therefore be carefully regulated. The gas is always contaminated with chlorine, and if the evolution has been tumultuous, may contain oxides of chlorine, which render it explosive. The dioxide of manganese undergoes no permanent change (p. 54).

Manufacture—3. *By heating manganate of sodium alternately in steam and air.*—This is an excellent process for the production of oxygen from air on a large scale.

The manganate is placed on the perforated shelf of a cylindrical retort, similar to a gas retort. Two pipes enter the retort at one end below the perforated shelf, one for the admission of steam, the second for air; at the other end there are two exit pipes above the charge, one opening directly into the air, which can be closed at pleasure, the other, also capable of being closed, connected with a condenser, and this with a gas-holder. The retort being charged and heated to a moderate red-heat, and the air-pipes being closed, steam is blown in at one end. In the current of steam the manganate decomposes as follows:—

$$\underset{\text{Sodium Manganate.}}{Na_2MnO_4} + \underset{\text{Water.}}{H_2O} = \underset{\text{Soda.}}{2NaHO} + \underset{\text{Manganese Dioxide.}}{MnO_2} + \underset{\text{Oxygen.}}{O}$$

The oxygen and excess of steam pass on through the condenser, where the steam is condensed, the former only reaching the gas-holder. When no more oxygen is evolved, the connections with the steam and gas-holder are cut off, the other two pipes are opened, and air is blown in. Re-oxidation then takes place as follows:—

$$2NaHO + MnO_2 + O = Na_2MnO_4 + H_2O.$$

Other methods of preparation or manufacture.—4. By heating manganese dioxide to redness in an iron retort, $3\,MnO_2 = Mn_3O_4 + O_2$. 5. By gently heating a paste of bleaching powder, to which a few grains of cobaltous chloride have been added, $2\,CaCl_2O = 2\,CaCl_2 + O_2$ (p. 54). 6. By electric decomposition of water, acidulated with sulphuric acid, oxygen appearing at the positive pole, $2\,H_2O = 2\,H_2 + O_2$. 7. By acting with diluted sulphuric acid on a mixture of bichromate of potassium and barium dioxide in the cold, $K_2Cr_2O_7 + 3\,BaO_2 + 7\,H_2SO_4 = K_2SO_4 + Cr_2 3\,SO_4 + 3\,BaSO_4 + 7\,H_2O + 3\,O_2$. 8. By heating nitrate of sodium, $2\,NaNO_3 = 2\,NaNO_2 + O_2$. 9. By heating barium dioxide, $2\,BaO_2 = 2\,BaO + O_2$, the baric oxide formed reabsorbing oxygen from air at a somewhat lower temperature, $2\,BaO + O_2 = 2\,BaO_2$. 10. By passing sulphuric acid over red-hot porcelain, $2\,H_2SO_4 = 2\,SO_2 + 2\,H_2O + O_2$, the bulk of the sulphurous anhydride is removed in the liquid form by compressing the mixed gases, the rest by water. 11. By heating sulphate of zinc, $2\,ZnSO_4 = 2\,ZnO + 2\,SO_2 + O_2$. 12. By heating subchloride of copper alternately in a current of air and of steam. *In air*, $2\,Cu_2Cl_2 + O_2 = 2\,Cu_2Cl_2O$; *in steam*, $2\,Cu_2Cl_2O = Cu_2Cl_2 + O_2$. 13. By dialysis of air through thin sheet india-rubber. 14. By repeated solution of air in water under increased, and expulsion by diminution of, pressure. 15. By the decomposition of carbonic anhydride by the green parts of plants under the influence of light. 16. *Brins' Process.*—By heating barium monoxide, BaO, to 700° C., and alternately exposing it to the action of dry air, free from carbonic anhydride, under a pressure of about 10 lbs. per square inch, and then subjecting it to a reduced pressure of about 1 to 2 lbs. per square inch. During the exposure oxygen is absorbed, while, during the period of reduced pressure, this oxygen is evolved.

Combustion.—In all chemical combinations which proceed without external aid, heat is evolved (p. 72). The amount of heat so evolved varies considerably, from very little or nothing, up to 34,462 units of heat evolved by the burning of 1 gramme of hydrogen in oxygen.

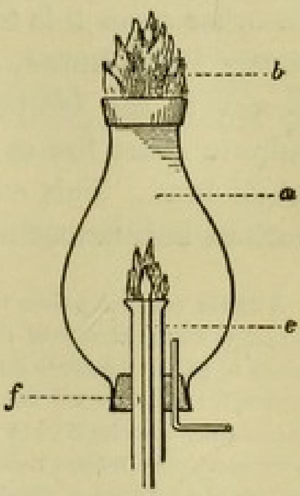
The amount of heat thus evolved in any given chemical action is always the same, whatever may be the rate at which the action proceeds, but the degree of temperature attained, or the intensity of the heat produced, may vary widely.

Thus, an iron wire, when burning in oxygen, not only evolves much heat but the temperature attained by it is very great, as illustrated by the fact that the globules of melted oxide, falling from the wire, burn themselves into the glazing of the plate on which the gas-jar stands, although the surface of the plate may be covered with a layer of water half-an-inch deep. If, however, the same weight of wire is allowed to rust in air, its temperature never rises sensibly above that of its surroundings, yet the *amount* of heat ultimately evolved will be as great as in the previous instance. The possibility of thus increasing the temperature by increasing the *rate* of combustion is practically made use of in our ordinary blow-pipes in the blast furnaces for smelting iron, &c., and finds its highest expression in the oxy-hydrogen blow-pipe.

There is, however, a limit to the intensity of heat or temperature. This limit depends (1) upon the units of heat evolved in the combustion; (2) the specific heats of the resulting bodies; and (3) sometimes, but not always, upon the temperature of dissociation of the latter.

Whenever the temperature produced during chemical action is sufficiently high, light is also emitted, and the phenomenon is then called *combustion*. Combustion, in its widest sense, may then be defined as the chemical combination of two or more substances, attended by the evolution of light and heat—as, for example, antimony burning in chlorine, copper in sulphur vapour, or phosphorus in oxygen.

In the case of all combustions taking place in atmospheric air (that is to say, of all combustions, the practical object or result of which is the production of light and heat) oxygen plays a part, and this term, "combustion," is therefore not unfrequently used in a somewhat restricted sense, meaning the chemical combination of some substance with oxygen, accompanied by the emission of light and heat. Two substances at least are necessary to bring about the production of heat and light by their combination, and, as in all chemical action, they must be in actual contact. In the case of a solid and a gas, contact can only take place at the surface of the solid; in the case of two gases, at the point where one gas issues into the other. Hence, in the case of the solid and the gas (say coke and air), the heat and light produced appear to proceed entirely from the solid—in the case of the two gases (say coal-gas and air), from the jet of the one gas issuing into the other. The body from which the heat and light appear to proceed is termed the combustible, the other body in which the combustion takes place being then termed the supporter of combustion. This division is, however, not strictly correct, inasmuch as both substances are equally necessary to the chemical action which results in this production of light and heat, and each in turn may be brought under conditions by which the heat and light appear to proceed from it alone. Nevertheless, as in all combustions which take place in atmospheric air, the heat and light appear to proceed, not from the oxygen, but from the substance combining with it, the division into "combustibles" and "supporter of combustion" may be a useful one. In this sense, then, oxygen is called a *supporter of combustion*, the substance combining with it the *combustible*.



The reversibility, so to speak, of these terms can be easily demonstrated in the case of two gases. (It is obviously not possible in the case of a solid and a gas.) A jet of coal-gas, for example, issuing into atmospheric air, may be lighted, and will continue burning as long as there is air present; but, on the other hand, a jet of air issuing into an atmosphere of coal-gas, may in its turn be lighted, and will continue burning as long as it is surrounded by an atmosphere of coal-gas.

In the above figure, let *a* represent a glass chimney, such as is used in a petroleum lamp. The lower end of the chimney is closed by a doubly-perforated cork, through one opening of which passes a short metal tube, about ¼-inch in diameter, and open at both ends; through the other opening passes a narrow glass tube bent at right angles. Round the upper end of the lamp-chimney is placed a broad ring of brass or copper foil, projecting some distance above. The whole apparatus is supported in an upright position, the bent glass tube is connected with a coal-gas supply, and this being turned on, the gas is lighted at the top of the chimney, when, if the supply is adequate, a large Bunsen flame will be obtained, *b*. If now a small gas jet, *e*, burning at the top of a long narrow tube, be passed up the wider metal tube, *f*, into the lamp-chimney, it will be found that as soon as the little jet appears above the mouth of the metal tube, the air ascending in this tube will take fire and burn with a pale, scarcely luminous flame, and will continue to burn even after the small gas-jet, *e*, is withdrawn. If we push the small gas-jet through the air-flame into the coal-gas, it is at once extinguished (coal-gas being unable to burn in an atmosphere of coal-gas), but is rekindled on slowly drawing it back into the interior of the air-flame (where it again meets with oxygen). We can by this experiment show at one and the same time (1) coal-gas burning in air; (2) air burning in coal-gas; and (3), again, coal-gas burning in air.

All substances have to be heated to a certain temperature before they begin to burn. This temperature has been termed the *temperature of ignition*, and varies widely for different substances. In some cases the temperature of ignition of a substance lies below the ordinary temperature; when this is the case, it takes fire as soon as it comes into contact with air. Such a substance is said to be spontaneously inflammable. In other cases this temperature is but little above the ordinary temperature. Phosphorus, *e.g.*, takes fire a little above 44°. In most cases, however, the temperature of ignition is considerably higher. Thus, sulphur takes fire at a temperature of 250°, while marsh gas requires a white heat. This considerable range of the temperature of ignition of various substances may be well illustrated as follows:—

A fairly red-hot poker will readily ignite a gas-jet or a Bunsen burner, but will no longer ignite it when at a dull red heat only. In this condition, however, the poker will ignite a piece of paper. Before long it will have cooled below the temperature of ignition of paper, and will refuse to set fire to it, but will readily explode a small heap of gunpowder. The poker may now be cooled by waving it in the air, or dipping it for a moment into water, and a temperature is soon reached when it is no longer able to explode gunpowder; but if it now be introduced into a small glass jar, having some bisulphide of carbon at the bottom, the vapour of this volatile liquid will at once take fire, and the poker must be cooled considerably before it ceases to ignite the vapour. But even at this temperature a piece of phosphorus will, on being touched with the poker, immediately burst into flame.

In most instances, when once the substance has begun to burn, it will continue burning; the heat evolved by the combustion being sufficient, and more than sufficient, to keep up the temperature. This is a point of great importance, if combustion is to go on, and it may be interfered with in various ways. A great deal depends upon the physical condition of the burning substance. A compact solid, which offers but a small surface to the action of the oxygen, and is at the same time a good conductor of heat, will often cease to burn because the heat is carried away by conduction faster than it is produced; the temperature of the substance sinks below the temperature of ignition, and extinction follows. An iron wire, raised to a white heat in air, begins to burn, but combustion very soon ceases when we withdraw the external source of heat. If, however, we plunge the burning wire into pure oxygen, we increase the rate of combustion; heat is now produced faster than it is lost, and the wire continues to burn. A similar effect is produced by increasing the points of contact by subdivision; finely divided iron, *e.g.*, becomes even spontaneously inflammable. Other substances behave in a like manner. On the principle that by cooling a burning substance below its temperature of ignition, it may be extinguished, is based the miners' safety-lamps of Davy and others, and the various safety-jets, &c.

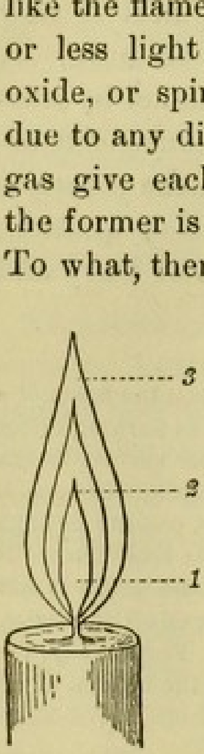
If we press a piece of moderately fine iron or brass wire-gauze down upon the flame of a candle or a Bunsen burner, it will be found that, while the flame continues burning below the gauze, no flame appears above it. If now we apply a light to the upper surface of the gauze, a flame appears over the flame below, proving that a quantity of combustible gas is passing through the gauze. The explanation is simple. The burning gases, passing through the meshes of the metallic gauze, part with their heat to the metal, their temperature is reduced below the point of ignition, and combustion ceases. As long as the gauze is not rendered too hot (nor its meshes injured) by the flame below, this cooling effect continues, but the flame will pass through the gauze if this becomes hot enough. Fortunately, the temperature of ignition of marsh gas (fire-damp) is a white heat, among the highest of all gases, and no great degree of cooling is necessary to extinguish its flame.

The following table will be of interest in connection with the foregoing remarks:—

						Heat-units.
1	gramme of	hydrogen	when burnt in	oxygen	evolves	34,000
1	,,	sulphur	,,	,,	,,	2,300
1	,,	carbon	,,	,,	,,	8,000
1	,,	phosphorus	,,	,,	,,	5,747
1	,,	iron	,,	,,	,,	1,575
1	,,	antimony	,,	chlorine	,,	707
1	,,	copper	,,	sulphur	,,	285

Flame.—On observing the appearance produced by a variety of combustibles, a great difference will be noticed as regards their manner of burning. An ordinary coal fire, when first lighted, shows a considerable amount of flame, but as time goes on this will become less and less, until at last the grate may be filled with a mass of red-hot coal, giving out much heat, but entirely without flame. Again, a candle burns with flame, an iron wire without flame. In what does this difference consist? What is flame? Flame is burning gas, and all combustible substances which are gases, or yield volatile combustible products, when heated, burn with a flame. On the other hand, substances which are neither volatile themselves, nor yield volatile combustible products, when heated, burn without flame.

Among flames themselves great differences are also observable. Some, like the flame of a candle, of an oil-lamp, or of coal-gas, give out more or less light; others, like the flame of burning hydrogen, carbonic oxide, or spirit, give scarcely any light at all. This difference is not due to any difference in temperature, for while olefiant gas and marsh gas give each a flame, the temperature of which is sensibly the same, the former is a brightly luminous flame, the latter almost non-luminous. To what, then, is this difference in luminosity due? The most probable explanation appears to be that of Professor Frankland, according to whom a non-luminous flame is produced by the burning of a gas of low density, a luminous flame by the burning of a gas of high density. Thus hydrogen, when burnt under ordinary atmospheric pressure, is non-luminous; whilst, when burnt under a pressure of twenty atmospheres or more, it becomes sensibly luminous. Our ordinary luminous flames are due chiefly to the burning of hydro-carbons of great density.



The hitherto generally received explanation, according to which the luminosity of a flame is due to the suspension of solid particles which become intensely heated, and emit light, is open to objection, though apparently furnishing a ready explanation of the phenomenon. That, however, intensely-heated solids emit much light is demonstrated by the heating of carbon by means of electricity in the various electric lights, of lime in the oxy-hydrogen flame, or of a spiral of platinum wire in a hydrogen or a Bunsen flame, &c.

All flames, with few exceptions, are hollow. This may be best seen in a candle flame which, on investigation, will be observed to consist of—(1) a central cone of unburnt gas; (2) a luminous envelope of burning gas or zone of incomplete combustion; (3) a non-luminous envelope of burning gas or zone of complete combustion—(2) and (3) are often called *inner* and *outer flames*, or also the *reducing* and *oxidising flames* in reference to their properties.

These parts of a flame may easily be shown in various ways. A platinum wire remains cool in the inner cone, and is most strongly heated in the outer flame. A piece of wire-gauze pressed down on the flame will show the inner cone and luminous envelope very distinctly.

If one end of a small tube be inserted in the interior of the flame, some of the unburnt gases may be withdrawn and ignited at the other end.

Many substances, such as a candle, in burning, disappear entirely from our sight. What has become of these combustibles? The matter of which they consist cannot have been destroyed nor altered in weight. It has only been changed by its union with the oxygen of the air into invisible gaseous compounds. In reality these gaseous products weigh more than the combustible which has disappeared, for they contain, in addition to the elements of the combustible, the oxygen which has been the means of their combustion (p. 4).

If we burn a candle in a long glass-tube, the top of which is filled with fragments of caustic soda, kept in position by means of a plug of wire-gauze while air is drawn through the tube by means of an aspirator, it will be found that, as the candle burns away, the apparatus constantly increases in weight, the caustic soda absorbing the products of the combustion of the candle (carbonic acid and water).

Oxides and Salts.—At least one oxygen-compound of every element, except fluorine, is known, and in the case of some elements many more than one are formed. All these oxygen-compounds are called *oxides*, and constitute a large and important class of substances. According to fairly well-marked characteristics, they may be divided into three groups, viz.:—

1. Oxides which alone, or in combination with water (when they are termed *hydroxides* or *hydrated oxides*), yield, with acids, the compounds termed salts. These oxides are called *bases*. Their hydroxides, when soluble in water, impart to it a peculiarly nauseous taste and soapy feeling; they turn yellow turmeric paper brown, and are without action on blue litmus, but, by neutralising the effect of any acid, they restore the blue colour to litmus which has been reddened by an acid. All basic oxides are oxides of metals.

2. Oxides which, in combination with water, yield compounds possessing, when soluble, a more or less sour taste, like vinegar, are termed *anhydrides** or *acid-forming oxides*. Their compounds with water are termed *acids*.

As this nomenclature does not embrace acids which contain no oxygen, a more general definition of an acid may be here given in order to avoid confusion later on. An acid, then, is a compound, "containing one or more atoms of hydrogen which become displaced by a metal when the latter is presented to the compound in the form of a hydrate." †

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* 'αν, *not*; ὕδωρ, *water*

† Frankland.

An acid containing only one atom of displaceable hydrogen is termed *monobasic*, if it contains more than one atom so replaceable, it is termed *polybasic* (di-, tri-basic, &c.)

Acids which contain oxygen may also sometimes be conveniently represented as containing, according to their basicity, one or more groups of the radical *hydroxyl* $(H\,O)'$, the hydrogen of which is replaceable by a metal under the above-named conditions.

These acids, when soluble in water, turn blue litmus red and are without action on turmeric.

If an element yields two oxygen acids, the one containing the higher proportion of oxygen is usually designated by a name ending in *ic*, the name of the acid containing the less proportion of oxygen ending in *ous*; as, for example, chlor*ic* acid $H\,Cl\,O_3$, and chlor*ous* acid $H\,Cl\,O_2$. Should an element yield more than two acids the affix *ic* or *ous* is retained, and the syllables *per* and *hypo* prefixed according as the compound contains more than the *ic* or less than the *ous* compound, as *per*chlor*ic* acid $H\,Cl\,O_4$, *hypo*chlor*ous* acid $H\,Cl\,O$. The various basic oxides of one and the same metal are distinguished in a similar manner, *e.g.*, mercur*ic* or mercur*ous* oxide. The non-metals, with one exception, and some of the metals yield acid-forming oxides.

By the mutual action of acids and bases, compounds termed *salts* are formed, *e.g.*,

$$\overset{\text{Zinc Hydrate.}}{Zn\,(H\,O)_2} + \overset{\text{Sulphuric Acid.}}{H_2\,SO_4} = \overset{\text{Zinc Sulphate.}}{Zn\,SO_4} + \overset{\text{Water.}}{2\,H_2\,O.}$$

The final result of this and similar reactions is the replacement of the hydrogen of the acid by the metal, and a *salt* may accordingly be defined as an acid in which the hydrogen is replaced by a metal.

These salts may be formed in various other ways. The following are typical examples :—

$$\overset{\text{Zinc.}}{Zn} + \overset{\text{Sulphuric Acid.}}{H_2\,SO_4} = \overset{\text{Zinc Sulphate.}}{Zn\,SO_4} + \overset{\text{Hydrogen.}}{H_2.}$$

$$\overset{\text{Zinc Oxide.}}{Zn\,O} + \overset{\text{Sulphuric Acid.}}{H_2\,SO_4} = \overset{\text{Zinc Sulphate.}}{Zn\,SO_4} + \overset{\text{Water.}}{H_2\,O.}$$

The names of salts of acids ending in *ic* have the termination *ate*, while those formed from acids ending in *ous* terminate in *ite*; thus, the salts of perchlor*ic*, chlor*ic*, chlor*ous*, and hypochlor*ous* acids are termed respectively perchlor*ates*, chlor*ates*, chlor*ites*, and hypochlor*ites*.

3. Oxides, which, when acted upon by hydrochloric acid, give rise to the formation of peroxide of hydrogen or chlorine, *e.g.*,

$$\underset{\text{Peroxide.}}{\overset{\text{Barium}}{}}\!\!\!\!\!\!\!\!\!\overset{}{BaO_2} + \overset{\text{Hydrochloric Acid.}}{2HCl} = \overset{\text{Barium Chloride.}}{BaCl_2} + \overset{\text{Peroxide of Hydrogen.}}{H_2O_2}.$$

$$\overset{\text{Manganese Peroxide.}}{MnO_2} + \overset{\text{Hydrochloric Acid.}}{4HCl} = \overset{\text{Manganese Dichloride.}}{MnCl_2} + \overset{\text{Chlorine.}}{Cl_2} + \overset{\text{Water.}}{2H_2O}.$$

These are called *peroxides;* they contain less oxygen than acid-forming oxides, but more than the basic oxides of the same elements, and usually part with a portion of their oxygen with great readiness. They may be used as oxidising agents or for the preparation of oxygen.

OZONE.

(*ὄζων, smelling*) $O_3 = 48$. *Gas at ordinary temperatures; liquid at* − 105° *under* 125 *atmospheres pressure. Specific gravity,* 1·658 (*air* = 1); 24 (*H* = 1).

Occurrence in Nature.—Ozone is found in traces in the atmosphere, more especially over the sea and in the open country, rarely in the air of towns, and sometimes occluded in some blue varieties of fluor-spar.

Physical Properties.—Ozone is at ordinary temperatures and pressure a bluish gas, its colour being visible in a column several feet in length. At considerable pressures it assumes a dark blue colour. It liquefies under the conditions above stated, forming a dark blue liquid. If rapidly compressed it explodes violently. It possesses a peculiar odour resembling somewhat that of chlorine or phosphorus (phosphorous odour, *see below*), which is noticeable in air containing not more than one volume in 500,000. It is but very slightly soluble in water, and is gradually destroyed in contact with it. Its absorption spectrum contains eleven bands.

Chemical Properties.—Ozone has never been prepared in a pure state; and, even in its most concentrated form, is mixed with at least three volumes of oxygen. Ozonised oxygen occupies less bulk than the oxygen from which it is prepared, but on heating to 250° or 300° the original bulk is restored, and the heated gas contains no ozone. It is, even at ordinary temperatures, an extremely active oxidising agent. It oxidises most non-metals, all metals (except gold and platinum and its allied metals), many oxides and salts, most organic matters, and, among these, cork and india-rubber.

When passed over manganese and other peroxides at ordinary temperatures, it is destroyed and converted into ordinary oxygen.

When made to act on a solution of potassium iodide, iodine is liberated. The ozonised oxygen does not diminish in bulk, and the amount of iodine liberated is equivalent to an amount of oxygen equal in volume to the diminution suffered by the oxygen during ozonising; the residual gas is ordinary oxygen.

Oil of turpentine, which does not appreciably dissolve ordinary oxygen, removes all ozone from ozonised oxygen, the gas diminishing in volume by twice the shrinkage during ozonising.

From this it appears that in ordinary oxidising effects only one-third of the ozone is active, and that ozone under such circumstances breaks up into a molecule and an atom of ordinary oxygen, this atom in the free or nascent condition possessing highly active properties. The molecule of ozone, therefore, consists of three atoms. This conclusion is confirmed by the density of the gas derived from its rate of diffusion, namely, 24. Hence, ozone is nothing else than an allotropic modification of oxygen.

In the formation of ozone the heat reaction is negative (p. 72), 355·5 heat units being absorbed during the production of 1 gramme.

Distinguishing Tests. — Ozone has a peculiar odour, turns iodized starch paper blue, paper impregnated with tincture of guaiacum resin blue, paper moistened with solution of sulphate of manganese or thallium brown, while paper stained black by sulphide of lead is turned white. It oxidises mercury and even very minute traces tarnish the metallic surface and make it adhere to glass; it also oxidises silver. Paper moistened with chloride of gold is turned violet by it. These three last are characteristic tests.

Physiological Action. — Ozone renders breathing difficult, powerfully irritates and inflames the mucous membranes of the air-passages, and is rapidly fatal to small animals.

Production and Preparation.—1. *By the slow oxidation of phosphorus and of various essential oils*, peroxide of hydrogen being also produced.

2. *By the action of the silent electric discharge on dry air or oxygen.* Ozone is best prepared from air or oxygen by means of a Siemens' tube. This apparatus consists of a double tube, the inner tube (through which a current of cold water may be kept constantly passing) is coated on its outer surface with tinfoil, the outer tube being similarly coated. Air or oxygen is slowly passed between the two tubes, while their respective coatings are connected with the wires from a powerful induction coil.

At the best, oxygen can only be made to contain from 15 to 25 per cent. of ozone. All contact of the ozonised oxygen with organic matter, such as cork or india-rubber, must be avoided.

HYDROGEN.

(*ὕδωρ, water, and γεννάω, I produce*) $H = 1$; $H_2 = 2$. *Gas at ordinary temperatures. Calculated critical temperature* −240°, *and calculated critical pressure* 13·3. *Specific gravity*, 1·0 (H=1); 0·0693 (*air*=1); *of liquid hydrogen, probably* 0·12 (*water*=1). *Monad.* 11·19 *litres weigh* 1 *gramme.*

Occurrence in Nature.—Hydrogen occurs free in the gases of active volcanoes, in nebulæ, in the atmospheres of the fixed stars and of the sun, and occluded in meteoric iron and in certain minerals (salt, coal). It forms $\frac{1}{9}$ by weight of water. It is very widely diffused, and abundant in organic substances, *i.e.*, in vegetable and animal matter, in combination with carbon.

Physical Properties.—Hydrogen, under ordinary conditions, is a colourless, tasteless, inodorous, gas, which has not yet been liquefied; its supposed liquefaction in 1878 has now been proved fallacious.

Hydrogen follows Boyle's law at moderately high pressures, but departs from it at very high pressures, thus, at 1015 atmospheres it is only reduced $\frac{1}{628}$ of its volume, instead of $\frac{1}{1015}$.

It is sparingly soluble in water, 100 vols. of which absorb 1·93 vols. between 0° and 20°, the coefficient of solubility remaining constant within these limits of temperature.

Hydrogen is absorbed by certain metals to a remarkable extent.

Thus, wrought iron will absorb an equal volume of hydrogen. Copper, silver, gold, and platinum absorb more or less considerable quantities (from 0·2 to 1 vol.), even at high temperatures. Meteoric iron has been found to contain very large quantities of occluded hydrogen. But the absorptive power of palladium for hydrogen is in enormous excess of any of the foregoing. Thus, at ordinary temperatures palladium foil has been shown to absorb 376 vols., at 97° 346 vols., at 245° 526 vols.; while electrolytically-deposited palladium absorbs, when heated in hydrogen to 100°, 982 vols., or 0·723 per cent. of its weight, retaining the greater portion of the gas even *in vacuo*.

Hydrogen is specially characterised by its low specific gravity, being in fact the lightest of all known substances.

It is nearly 14½ times lighter than air, 11,160 times lighter than water, 87,700 times lighter than iron, 151,700 times lighter than mercury, 240,000 times lighter than platinum. The difference between its specific gravity and that of air (1 : 14½) is greater than the difference between the specific gravities of water and mercury (1 : 13½). The *calculated* specific gravity of hydrogen is 0·0691 (air = 1), as against 0·0693 (air = 1), the specific gravity *found* by experiment. The former number is probably the most accurate, and is calculated as follows:—In water 2 vols. of hydrogen are united with 1 vol. of oxygen, their relative weights being as 1 : 8 exactly, or for equal volumes of hydrogen and oxygen, as 1 : 16 exactly; now, specific gravity of oxygen by experiment = 1·10563 (air = 1), hence, theoretically specific gravity of hydrogen $= \frac{1·10563}{16} = 0·069101$.*

For this reason it has been selected by chemists as the standard or unit with which comparison is made of the specific gravity of all gases, both elementary and compound, particularly as this also bears a simple relation to their molecular weights, as compared to the same standard. This low specific gravity is strikingly illustrated by its high rate of diffusion, its comparative inability to conduct sound, and the ease with which it can be poured *upwards* from one vessel into another. Its coefficient of expansion = 0·0036678 under constant pressure (Regnault) between 0° and 100°. Its *specific heat* = 3·4090 under constant pressure (Regnault). Its *absolute index* of refraction = 1·000138. Its refractive power is greater than that of any other known substance, and is more than six times as great as that of air at the same density. It is eminently electro-positive.

Chemical Properties.—Hydrogen is an inflammable gas burning in air, with a very hot and scarcely luminous flame, which, however, becomes luminous at a pressure of 10 atmospheres. The product of its combustion in air is water. By the burning of 1 gramme of hydrogen to water, 34,462 units of heat are evolved. It will not support the combustion of a taper, but oxygen and chlorine will burn in it. If the gas before ignition is mixed with oxygen, the combustion may spread instantaneously through the whole mixture, giving rise to an explosion which is most violent when the proportion of hydrogen to oxygen is that of 2 vols. to 1, the proportion in which the two gases unite to form water. With air the explosion is most violent when the gases are in the proportion of 2 vols. hydrogen to 5 vols. air, but it is always less violent than with the equivalent proportions of pure oxygen. Hydrogen may be ignited in air or oxygen by a flame, by a red-hot solid, by the electric spark, and also by the agency of spongy platinum, or even very clean platinum foil and wire, either slowly or quickly, according to the condition of the platinum and the manner in which the experiment is made. Platinum black, which is platinum in its

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* *N.B.*—$\frac{1·10563}{15·96} = 0·06927$.

most finely divided state, brings about the combination instantly. If hydrogen be allowed to impinge upon a piece of spongy platinum, this first begins to glow, and finally becomes so hot that the hydrogen is ignited.

One of its chief chemical characteristics is its strong affinity for chlorine. With chlorine, hydrogen unites instantaneously under favourable conditions. If equal vols. of hydrogen and chlorine be mixed and exposed to diffused daylight, the green colour of the chlorine gradually disappears; if exposed to direct sunlight or powerful artificial light, combination ensues instantly, and with explosion, hydrochloric acid being formed. Hydrogen will burn in bromine, forming hydrobromic acid when a little air is present, but will not burn in iodine vapour. It also combines directly, but with difficulty, and at a high temperature only with sulphur, and at very high temperature, with carbon, forming acetylene. This last is one of the reactions by means of which chemists have broken down the boundary between so-called inorganic and organic compounds. It forms, however, numerous and important compounds with all the non-metals.

Hydrogen is a powerful *reducing agent*, many metallic oxides yielding up their oxygen to it at a red heat, *e.g.*:—

$$\begin{array}{ccccccc} \text{Cupric Oxide.} & & \text{Hydrogen.} & & \text{Copper.} & & \text{Water.} \\ Cu\,O & + & H_2 & = & Cu & + & H_2\,O, \end{array}$$

water being formed, and the metal left in a finely divided state.

It also decomposes some sulphides and chlorides of the metals at a higher temperature, with separation of the metal and formation of sulphuretted hydrogen or hydrochloric acid respectively, *e.g.*:—

$$\begin{array}{ccccccc} \text{Antimony Trisulphide.} & & \text{Hydrogen.} & & \text{Sulphuretted Hydrogen.} & & \text{Antimony.} \\ Sb_2\,S_3 & + & 3\,H_2 & = & 3\,H_2\,S & + & Sb_2 \end{array}$$

$$\begin{array}{ccccccc} \text{Ferrous Chloride.} & & \text{Hydrogen.} & & \text{Hydrochloric Acid.} & & \text{Iron.} \\ 2\,Fe\,Cl_2 & + & H_2 & = & 2\,H\,Cl & + & Fe_2. \end{array}$$

Nascent hydrogen, or the hydrogen as absorbed, for example, in palladium, has very great reducing power, even at ordinary temperatures. Ferric salts are reduced by it to the ferrous condition; nitric acid to ammonia, &c.

Physiological Action.—It is not poisonous, but cannot be respired pure, and brings about loss of muscular power and extreme weakness of the voice.

Great care should be taken that the hydrogen intended to be inhaled is pure, more particularly that it is free from arseniuretted hydrogen, with which hydrogen evolved from ordinary zinc is very often contaminated.

Distinguishing Tests.—A very light, quickly diffusing, colourless, tasteless, and (when pure) inodorous gas, burning with an *almost invisible* very hot flame, water being formed, and exploding violently when mixed with about half its volume of oxygen, with formation of water only. Almost insoluble in water or other ordinary solvents.

Preparation.—Hydrogen is usually prepared from water or sulphuric acid by the action of certain metals.

1. *By the action of Sodium on Water.*—When a piece of the metal sodium is thrown upon water, it floats to and fro upon the surface, melts, rotates rapidly, assuming a spherical shape, its movements being accompanied, and in fact caused, by a brisk evolution of hydrogen. If the water has been coloured by reddened litmus, the colour will be changed to blue, owing to the formation of a *base* (p. 93), viz., the hydrated oxide of sodium (soda):—

Sodium.		Water.		Sodium Hydrate.		Hydrogen.
Na_2	+	$2H_2O$	=	$2NaHO$	+	H_2.

If a small piece of sodium be depressed below the surface of the water by means of a piece of wire-gauze bent into the shape of a spoon, the hydrogen may be collected by holding a tube filled with water over the gauze. The experiment so conducted is free from danger of explosion, provided a small piece of clean sodium only is taken.

The process is interesting as a chemical reaction, but is not adapted for preparing any quantity of hydrogen, owing to the expense of the sodium and the danger attending its use.

2. *By the action of Iron on Water.*—Iron and some other metals, which, though not like sodium, decomposing water at ordinary temperatures, will decompose it at a red heat. In the case of iron, if steam be passed through an iron tube which contains iron wire or iron filings, and which is heated to a red heat, the steam is decomposed, magnetic oxide of iron is formed, hydrogen is set free and passes on, and may be collected by displacement of water in a pneumatic trough. This is a cheap method for preparing hydrogen, and has been used as a process of manufacture for large quantities of the gas. The gas obtained is not pure.

Iron.		Water.		Magnetic Oxide of Iron.		Hydrogen.
$3Fe$	+	$4H_2O$	=	Fe_3O_4	+	$4H_2$.

3. *By the action of Zinc on Sulphuric Acid.*—This is by far the most

convenient method of preparing hydrogen. Sulphuric acid, diluted with three to four times its volume of water, is poured upon *granulated* zinc[*], whereupon a brisk evolution of hydrogen takes place, zinc sulphate being simultaneously formed:—

$$\overset{\text{Zinc.}}{Zn} + \overset{\text{Sulphuric Acid.}}{H_2SO_4} = \overset{\text{Zinc Sulphate.}}{ZnSO_4} + \overset{\text{Hydrogen.}}{H_2}.$$

The simplest form of apparatus is a Woulff's bottle, which has two necks fitted with perforated corks; through one of these a thistle-funnel passes almost to the bottom of the bottle; through the other a right-angled delivery tube which only just reaches below the neck. The zinc is placed at the bottom of the flask, and the dilute acid poured upon it, or the zinc may be just covered with water, and strong sulphuric acid added in small quantity, but this is not so advisable. Great care must be taken that all air has been driven out of the apparatus by allowing the evolution of gas to go on for some time before the gas is ignited or collected, in order to avoid an explosion. If both zinc and sulphuric acid are pure, the resulting hydrogen is pure.

Commercial zinc and sulphuric acid contain arsenides, phosphides, and sulphides which give rise to gaseous compounds of hydrogen, viz.:—arseniuretted hydrogen (AsH_3), phosphuretted hydrogen (PH_3), and sulphuretted hydrogen (SH_2), each possessing its peculiar odour which it imparts to the gas. The first two impurities may be removed by passage of the gas through U-tubes containing mercuric chloride ($HgCl_2$), or silver nitrate ($AgNO_3$), the latter by means of caustic potash (KHO).

Manufacture—4. *By the passage of steam over charcoal at a dull red heat.*—If the temperature is carefully regulated, hydrogen and carbonic anhydride only are formed, the latter being absorbed by transmission through lime:—

$$\overset{\text{Water.}}{2H_2O} + \overset{\text{Charcoal.}}{C} = \overset{\text{Hydrogen.}}{2H_2} + \overset{\text{Carbonic Anhydride.}}{CO_2}.$$

Other Modes of Production—5. *By the action of Zinc on Hydrochloric Acid.*—The latter must be sufficiently diluted to prevent its fuming. $Zn + 2HCl = ZnCl_2 + H_2$. 6. *By the action of Iron on Sulphuric Acid.*—$Fe + H_2SO_4 = FeSO_4 + H_2$. The gas is always very impure, and contains hydrogen compounds of carbon. 7. *By the action of Iron on Hydrochloric Acid.*—$Fe + 2HCl = FeCl_2 + H_2$. 8. *By the action of Zinc (or of Zinc and Iron) on Caustic Potash.*—$Zn + 2KHO = H_2 + K_2O\,ZnO$. 9. *By the action of Aluminium on Caustic Potash.*—$Al_2 +$

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[*] Zinc, which has been melted and poured in a thin stream into water, by which treatment it is separated into small lumps of irregular shape, which present a considerable surface to the acid.

$6KHO + 6H_2O = Al_2O_3 3H_2O + 6KHO + 3H_2$. 10. *By the action of Caustic Alkalies on Aldehydes e.g.*—$C_2H_4O + KHO = KC_2H_3O_2 + H_2$. 11. *By heating Formate of Potassium with Potassic Hydrate.*—$KCHO_2 + KHO = K_2CO_3 + H_2$. This preparation is interesting as having been used in the liquefaction of hydrogen. 12. Pure hydrogen is best prepared by electrolytic decomposition of water acidulated with about one-tenth of its volume of pure sulphuric acid; the positive pole consisting of an amalgam of zinc and mercury, the negative pole being a platinum plate.

WATER.

(*Aryan root, wad, to well or gush out**) $H_2O = 18$. $[H - O - H]$. *Percentage composition*, $H = 11{\cdot}11$; $O = 88{\cdot}89$. *Liquid at ordinary temperatures; boiling point*, 100°; *freezing point*, 0°. *Specific gravity of liquid*, 1 (*water* = 1); *of solid* (*ice*), 0·9175 (*water* = 1); *of gaseous* (*steam*), 0·625 (*air* = 1); 9 ($H = 1$). 1 *cubic centimetre of distilled water at* 4°*C. weighs* 1 *gramme.* 11·19 *litres of steam weigh* 9 *grammes.*

Occurrence in Nature.—Water is one of the most abundant and familiar compounds in nature. It occurs, in the solid form, as ice, snow, hail, and hoar-frost, in combination with many substances as *water of crystallisation*, &c., and in animal and vegetable matter; in the liquid form as dew, rain, spring water, river water, sea water, and mineral waters; in the gaseous form as steam, vapour, cloud, fog, mist. It is one of the products of the combustion of most organic matters, and of the respiration of animals.

Physical Properties.—Water, between 0° and 100°, is, when pure, a colourless, or, in greater masses, a blue, transparent, mobile, tasteless, and odourless liquid. At 0° it solidifies to a transparent, colourless, or, in larger masses, to a blue crystalline solid. It evaporates at all temperatures, and boils at 100°C. when the barometer stands at 760 mm.

Being one of the most widely diffused and most familiar substances in nature, and easily obtainable in a state of comparative purity, it has, for these and other reasons been selected as the chief unit of comparison for expressing the specific gravities of all known solids and liquids; its boiling point at the normal pressure of the atmosphere, and the melting point of ice have been chosen as fixed points of temperature from which all thermometers in use have been graduated.

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* Skeat.

In some respects, as will be seen immediately, it is, by no means, the most perfect of standards, owing to its somewhat anomalous behaviour to heat. Thus, although ice melts at a constant temperature,* water, if cooled gradually and kept very still, may be cooled to as low as −20° without solidification ensuing. The least disturbance is, however, sufficient to cause solidification to take place, and the temperature rises to 0°. Further, when water at 0° is heated, it contracts instead of expanding, and continues to contract up to 4°, from which temperature it commences to expand and goes on expanding regularly in a gradually increasing ratio up to 100°, when it boils. One volume of water at 0°C. becomes 0·9998 volume at 4°, 1·000 at 8°, and 1·043 at 100°. At 4°, therefore, it attains its maximum density, and at 8° occupies the same volume as it did at 0°.

Water in solidifying, instead of contracting, as is the case with most substances, expands $\frac{1}{11}$ of its volume. Ice is, therefore, lighter than water, and has a specific gravity of 0·9175 (water = 1), and, if formed in a confined space, exerts a pressure which no ordinary vessel can withstand. The crystalline structure of ice belongs to the hexagonal system, and appears in very varied forms in snow.

One cubic inch of water at 60° F., weighs 252·456 grains; 1 cubic foot weighs 997 (nearly 1,000) ounces; 1 cubic centimetre at 4°C. weighs 1 gramme (15·432 grains); and 1 cubic metre weighs 1 million grammes (1,000 kilos.) or 0·9842 ton (1 ton nearly).

Water evaporates at all temperatures. Steam, *at and above* 100°, is an invisible gas, but becomes visible as vapour on partial condensation in contact with air. It occupies 1,700 times (1,696 exactly), the volume of the water from which it is generated (1 cubic inch of water generates about 1 cubic foot of steam). Its specific gravity is 0·625 (air = 1).

Like most liquids, water is a bad conductor of heat. Its specific and latent heat have already been dealt with in chapter vi. Both solid and liquid, it is a bad conductor of electricity. Ice becomes electric on friction.

Chemical Properties.—Water, sometimes called monoxide of hydrogen, is a compound of oxygen and hydrogen. In 100 parts by weight, 88·88 parts of oxygen are combined, with 11·11 parts of hydrogen, a proportion which corresponds to 16 parts of oxygen united with

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* The melting point of ice, though sensibly constant under all ordinary conditions, is not so absolutely, but is lowered by great pressure. Thus, ice at 0°, when submitted to great pressure, in an hydraulic press, for example, can be pressed into a liquid, and solidifies again when the pressure is removed.

2 parts by weight of hydrogen. The volumetric relations corresponding to these weights are 2 volumes of hydrogen to 1 volume of oxygen; these three volumes, if the experiment is conducted at above 100°, condensing to 2 volumes of steam.

The facts thus briefly stated have been conclusively proved by the most rigid experimental methods, and are in complete consonance with the theory which asserts that the molecule of water contains 2 atoms of hydrogen, united with 1 atom of oxygen as expressed by the formula H_2O or $H-O-H$.

The following brief résumé of the more important of these experiments may suffice:—

1. If two platinum or carbon plates connected with the two poles of a Bunsen battery of three or four cells (say of one pint capacity each) are plunged into water, to which one-eighth of its volume of sulphuric acid has been previously added, a copious evolution of gas takes place. If the gases be collected separately, that which is evolved at the negative pole, is found to have twice the volume of that evolved at the positive pole, and the two gases may be respectively proved to be hydrogen and oxygen. If the gases are collected in the same vessel, a mixture is obtained, which explodes violently on ignition with formation of water.

2. It has already been shown (p. 98) that when hydrogen is burnt in air water is formed, and if 2 volumes of hydrogen be mixed with 1 volume of oxygen in a strong glass eudiometer over mercury (the whole being surrounded by a glass cylinder kept filled with the vapour from boiling amylic alcohol, so that the temperature of the mixed gases is 132°), and an electric spark be passed through the mixture, 2 volumes of steam are formed. Moreover, whatever be the relative volumes of the two gases, combination, when the mixture is ignited, always takes place in the proportion of 2 volumes of hydrogen to 1 volume of oxygen, the residual gas consisting, as the case may be, of oxygen or hydrogen, whichever gas has been present in excess of this proportion. If the eudiometer is not surrounded by a hot jacket, an enormous condensation ensues after combination, and the mercury fills the vacuum formed.*

3. If perfectly pure and dry hydrogen is passed over dry and pure cupric oxide, at a gentle red heat, water is formed by the union of the hydrogen with the oxygen of the cupric oxide.

$$\begin{array}{ccccccc} \text{Cupric Oxide.} & & \text{Hydrogen.} & & \text{Water.} & & \text{Copper.} \\ CuO & + & H_2 & = & H_2O & + & Cu. \end{array}$$

If this water be collected without loss and weighed, and the bulb containing the cupric oxide be also weighed before and after the experiment, then the loss of weight of the cupric oxide gives the quantity of oxygen by weight, which has combined with hydrogen to form the water collected, and the weight of hydrogen with which the oxygen has combined, is found by subtracting the loss of weight of the cupric oxide from the weight of the water. In this manner it has been proved that 88·88 parts by weight of oxygen combine with 11·11 parts by weight of hydrogen to form 100 parts by weight of water.

These three experiments are sufficient to prove the foregoing statements with regard to the composition of water.

Water is a very stable compound, but, like all compounds, is

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* 1,696 volumes of hydrogen unite with 848 volumes of oxygen to form water. In other words, 2,544 volumes of the mixed gases unite to form 1,696 volumes of steam, and these condense to 1 volume of water. Hence, a mixture of oxygen and hydrogen in the proportion in which they unite to form water, if ignited, undergoes a condensation of 2,544 volumes to 1.

capable of decomposition under certain conditions. In addition to its decomposition by electricity (electrolysis) the following may be mentioned:—

A. By heat. A sufficiently high temperature will cause the dissociation of water. Thus, if melted platinum is poured into water, a mixture of gases is evolved, consisting of oxygen and hydrogen in the proportion in which they form water.

B. By chemical attraction. 1. At ordinary temperatures in contact with water the alkali metals, potassium, sodium (also Cs, Rb, and Li), combine with its oxygen, hydrogen being evolved.

2. The same result is produced at a low red heat when steam is passed over carbon, the earthy metals, iron, zinc (also Co, Ni, Mo, Cr, V, Sn, Cd), and at a bright red heat in the case of antimony, bismuth, lead, and copper.

3. In the presence of an acid (hydrochloric or sulphuric) this decomposition takes place either at or a little above the ordinary temperatures with the earthy metals, iron, zinc (also Mn, Cd, Sn, Fe, Co, and Ni.—See preparation of hydrogen, p. 100).

4. Chlorine dissolved in water unites, under the action of sunlight, with its hydrogen, oxygen being evolved.

5. Trichloride (PCl_3) and pentachloride (PCl_5) of phosphorus decompose water, the phosphorus combining with the oxygen and the chlorine with the hydrogen.

Water, then, is an oxide of hydrogen, but possesses neither acid nor basic properties (p. 93) in the ordinary sense of these terms.

It combines with some elements (Cl and Br) forming compounds termed hydrates, readily decomposed by heat into water and the element. With basic oxides it forms compounds termed hydrates or hydroxides. In most cases these compounds, when heated, break up more or less readily into water and anhydrous oxide, but in some (hydroxides of the alkali metals and of barium) this decomposition cannot be effected by heat. The molecules of the alkaline hydroxides cannot, in fact, contain water, and, for the sake of analogy, it is assumed that in all these hydrates or hydroxides the molecule of water has suffered decomposition and is no longer present as such; thus:—

Potassium hydroxide,	$K_2O + H_2O = 2KHO$.
Sodium hydroxide,	$Na_2O + H_2O = 2NaHO$.
Barium hydroxide,	$BaO + H_2O = BaH_2O_2 = Ba(HO)_2$.
Calcium hydroxide,	$CaO + H_2O = CaH_2O_2 = Ca(HO)_2$.
Ammonium hydroxide,	$NH_3 + H_2O = NH_4HO = AmHO$.
Ferric hydrate,	$Fe_2O_3 + 3H_2O = Fe_2H_6O_6 = Fe_2(HO)_6$.

In some cases these hydroxides are capable of uniting with more water to form crystalline compounds, in which the additional water may be distinguished as water of crystallisation; thus:—

Crystallised barium hydrate, ... $BaH_2O_2, 8H_2O$.

It combines with many acid-forming oxides (anhydrides) with formation of the corresponding acids (p. 93)—

Nitric Anhydride.		Water.		Nitric Acid.
N_2O_5	+	H_2O	=	$2HNO_3$.

Sulphuric Anhydride.		Water.		Sulphuric Acid.
SO_3	+	H_2O	=	H_2SO_4.

Phosphoric Anhydride.		Water.		Metaphosphoric Acid.
P_2O_5	+	H_2O	=	$2HPO_3$.

In many cases the acid, when heated, breaks up, more or less readily, into anhydride and water; thus:—

Boracic Acid.		Boracic Anhydride.		Water.
$2BH_3O_3$	=	B_2O_3	+	$3H_2O$.

In others, part only of the water can be so expelled; thus, if ordinary phosphoric acid is heated, it breaks up as follows:—

Tribasic Phosphoric Acid.		Metaphosphoric Acid.		Water.
H_3PO_4	=	PHO_3	+	H_2O.

In others, again, this decomposition cannot be effected by heat at all.

Some acids are capable of combining with more water, forming compounds which may be viewed as hydrates or polybasic acids, breaking up more or less readily into water, and an acid of lower basicity; thus:—

$$PHO_3 + H_2O = H_3PO_4;\ H_2SO_4 + H_2O = H_4SO_5;\ H_2SO_4 + 2H_2O = H_6SO_6.$$

Water further forms compounds which, in every case, are destroyed by a moderate heat generally at or below 100°C. When present only in the crystalline compound, this water is often termed *water of crystallisation*, whereas, the water which is not bound to the crystalline form, and which generally requires a higher temperature for its expulsion, is often known as *constitutional* or *saline water*, and its place may often be taken by another salt with formation of a so-called double salt.

Cupric sulphate, $CuSO_4, 5H_2O$, when heated to 100°, loses its crystalline form and blue colour, four molecules of water being expelled; to expel the fifth molecule a temperature of 242° is required.

Magnesium sulphate, $MgSO_4, 7H_2O$, when heated to 100°C., loses five molecules of water, at 150° it loses an additional molecule, while, to expel the last, a temperature of 250° is necessary.

The place of this seventh molecule of water may be taken by a molecule of an alkaline sulphate with the formation of a double salt crystallising with six molecules of water, thus—$MgSO_4, K_2SO_4, 6H_2O$.

Some salts lose the whole or part of their water of crystallisation in moderately dry air, even at ordinary temperatures (such salts are said to *effloresce*);[*] many more lose it in vacuo or over sulphuric acid, and all do at 100°C. Other salts, when deprived of their water of crystallisation by heating, reabsorb it when exposed to moist air, or take it up again without previous solution when acted on by water. Thus gypsum ($CaSO_4\ 2H_2O$), when heated, loses its two molecules of water, but recombines with them when exposed to moist air or when mixed with water (plaster of Paris). Other salts, again, when exposed to moist air, attract moisture in indefinite proportions and liquefy in the water so attracted; such salts are called *hygroscopic*[†] or *deliquescent*,[‡] they *deliquesce*, as it is termed. These last may be used for drying gases.

Water constitutes, perhaps, the most universal solvent, being capable of dissolving a greater number and variety of substances than any other compound known.

It dissolves all gases, without exception, but in very varying quantity, according to the nature of the gas, the amount dissolved increasing with the pressure, but diminishing as the temperature rises. For gases of moderate solubility, the solubility increases in proportion to the pressure exerted by the dissolving gas.

With regard to its solvent action upon liquids, a question which has been but little studied, we need only remark that water does not dissolve some (oils, &c.); that it dissolves others in limited quantity (ether, acetic ether, chloroform); while, again, others dissolve in water in unlimited quantity, or, in other words, are miscible with it in every proportion (alcohol).

Some solids are also insoluble (all metals as such, for example); others, and that the greater number are soluble in water to a greater or less extent; while, lastly, some at certain temperatures are soluble in water in any proportion (nitrate of ammonia at 100°C.)

In regard to the second of these classes the following points may be noted:—As a rule the solubility of a substance increases with the temperature, sometimes in a ratio exactly proportional to the temperatures ($ZnSO_4$, $MgSO_4$); but more generally the solubility increases more rapidly than the temperature (KNO_3, $Ba(NO_3)_2$). In some cases the solubility is almost the same at all temperatures ($NaCl$); while in others the solubility even diminishes as the temperature rises (CaO, H_2O and many calcium salts). A most remarkable phenomenon is shown by sulphate of soda; the solubility of this salt at first increases with the temperature, reaches a maximum at 38°, after which the solubility diminishes. In most cases a solution which, at a higher temperature, has taken up or dissolved all the salt it is capable of dissolving (saturated solution), when cooled to a lower temperature deposits the salt, in excess of that which it is capable of holding at a lower temperature, in a crystalline form. Sometimes, however, this excess is not deposited but remains in solution, but in a very unstable condition; and if a speck of dust, but especially a solid particle of the salt held in solution is dropped in, the whole excess crystallises out in a very short time, the temperature rising perceptibly (latent heat of liquidity). Such a solution, which contains more salt in solution than under normal conditions it is capable of holding at the temperature at which it is, is called a supersaturated solution. The

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[*] Efflorescco, *I blossom out.*

[†] ὑγρος, *moist, and* σκοπεω, *I look.*

[‡] Deliquesco, *I liquefy.*

phenomenon is readily shown with either the sulphate or hyposulphite of sodium. A similar phenomenon is observed with some solids in a state of fusion; they refuse to solidify at temperatures at which they are ordinarily solid, solidification at once occurring when they are touched with a solid particle of the same substance (sulphur, phosphorus, gallium). This phenomenon is called superfusion.

Preparation of Pure Water.—For ordinary purposes water may be sufficiently purified by simple distillation—the first and last portions of the distillate being rejected, and only the middle portion, say three-fourths of the whole, collected.

For special purposes, and when absolutely pure water is required, the water to be distilled is first boiled for some time with a strongly acid solution of permanganate; it is then submitted to distillation, the first portion, say one-fifth of the whole, being, as before, rejected; or, better still, the water is distilled through red hot tubes containing oxide of copper, and redistilled, being the second time condensed and collected in vessels of pure silver or platinum and kept out of contact with air.

Distinguishing Tests.—A colourless, tasteless, inodorous, neutral, and non-inflammable liquid, which, on evaporation, leaves no trace of residue.

Natural Waters.—From a strictly chemical point of view any foreign substance dissolved, or held in suspension, in water must be looked upon as an impurity, and in that sense all natural waters are more or less impure. In this respect they may be ranged in the order of purity as follows:—rain water, and water from melting ice or snow, river and lake water, ordinary spring and well water, sea and mineral waters. Considered, however, in relation to its use for drinking and other domestic purposes, it is more or less misleading to call every such substance, dissolved or suspended, an impurity, but only such as are distinctly harmful should be regarded as such.

All non-poisonous mineral matters, then, unless they amount to say more than 50 grains per gallon, may as regards the potability of a water be as a rule disregarded. The only exception to be made is in regard to such mineral matters as are indicative of, or are derived from, organic matter with which the water may have been contaminated; these are chlorides and phosphoric acid, frequently derived from urine of men or animals, and nitrates and ammonia, derived from nitrogenised matter of similar origin.

For some domestic uses, as washing, for example, a water containing but little mineral matter, especially salts of lime and magnesia, is desirable, since these bases form insoluble salts with the fatty acids of soap, or, in familiar language, they *curdle* the soap. In this respect waters are divided into *hard* waters, containing much, and *soft* waters, containing little, of these in solution. A water may be considered soft if it contains less than 10, hard if more than 10, grains of carbonate of lime or its equivalent per gallon.

We distinguish between *temporary* and *permanent hardness* in water. *Temporary hardness* is due to carbonates of calcium or magnesium, which, although of themselves insoluble, are dissolved by water containing free carbonic acid. On boiling or on addition of lime-water they are precipitated, and the water is rendered softer. *Permanent hardness* is that due to calcium and magnesium salts, other than carbonates (chlorides, nitrates, or sulphates); such water can only be rendered soft by addition of sodium carbonate (washing soda), but not by boiling.

There are, of course, more distinctly poisonous mineral matters sometimes found in water, the presence of which, even in minute quantity, renders the water unfit for drinking. Lead is not unfrequently found in soft water which has been passed through lead pipes or stored in lead cisterns, and is often a little suspected source of lead poisoning. Copper and arsenic are also occasionally found in the waters of certain districts.

The chief impurities, however, to be guarded against are so-called organic impurities; these may be divided into two or, better, three heads:—

Vegetable Impurities.—These may be derived from plants growing in the water, vegetable matters, such as leaves falling into the water, chiefly in autumn, vegetable matter washed from the surface by rain or dissolved from the soil during the percolation of the water through it. Vegetable matter, when present in, relatively speaking, large quantity, is objectionable, but, when in moderate quantity, need not be objected to on the score of unwholesomeness, although it may render the water less pleasing to the taste and sight.

Animal Impurities.—These may be considered under two heads—(*a*) impurity derived from men and animals not suffering from any specific infectious disease, and (*b*) impurity derived from infected men or animals. There is reason to believe that contamination of the former kind (*a*), although objectionable and having an injurious effect on consumers of it by lowering their state of health, and rendering them more liable to infection, does not produce any specific disease, whereas, even excessively minute traces of the second (*b*) are liable to reproduce the disease in all those drinking the water. At present, chemists have no means of distinguishing between these two kinds of animal contamination, and it behoves us, therefore, to be careful to point out the possible, nay, almost certain danger, incurred in using a water in which animal contamination can be traced; such water is at all times objectionable, and may at any time become dangerous.

We cannot here enter at length into the complicated subject of water analysis, and must content ourselves with emphasising the points specially requiring attention as enumerated below.

Colour and smell of the water, hardness, lime and magnesia salts, presence or absence of nitrous acid, of phosphoric acid, of poisonous metals, of saline and albumenoid ammonia, of nitrates and chlorides, of organic carbon and nitrogen, amount of oxygen absorbed from permanganate, and character of the suspended matter.

As regards the quantities of these various matters permissible in a drinking water no definite rules can be laid down, but every water should be judged by the characters of the unpolluted water of the strata and district from which it is derived; chemists, as beforesaid, can only point out certain forms of pollution, the rest must be left to the Engineer or Medical Inspector.

PEROXIDE OF HYDROGEN.

$H_2O_2 = 34$. $[(HO)'_2]$—*Percentage composition* $O = 94{\cdot}12$; $H = 5{\cdot}88$. *Fluid at ordinary temperatures. Specific gravity,* 1·45 (*water* = 1).

Occurrence in Nature.—Peroxide of hydrogen is found in minute quantities in the atmosphere, especially after a storm.

Physical Properties.—Peroxide of hydrogen is a colourless, transparent fluid, scarcely distinguishable in appearance from water, but is less mobile and possesses a peculiar odour and taste. It is not frozen at $-30°$. It evaporates slowly in vacuo without decomposition. It is miscible with water.

Chemical Properties.—Peroxide of hydrogen is a very unstable compound, being decomposed into water and oxygen at from 15° to 20°, sometimes with explosion; organic substances, such as fibrin or blood itself, decompose it on mere contact. Mixed with water or with hydrochloric acid solution it is more stable.

Its chemical behaviour is in every respect remarkable. It behaves both as an oxidising and as a reducing agent. Thus, it oxidises arsenic to arsenic pentoxide (As_2O_5), sulphide of lead ($Pb\,S$) to the sulphate ($Pb\,SO_4$), and sulphurous anhydride (SO_2) to sulphuric acid (H_2SO_4), and liberates iodine from iodides; on the other hand, peroxide of lead in contact with it yields up oxygen, being converted into lead monoxide, the peroxide of hydrogen also yielding up oxygen, and being converted into water.

$$\begin{array}{ccccccccc} \text{Lead Peroxide.} & & \text{Hydrogen Peroxide.} & & \text{Lead Monoxide.} & & \text{Water.} & & \text{Oxygen.} \\ PbO_2 & + & H_2O_2 & = & PbO & + & H_2O & + & O_2 \end{array}$$

A similar reaction occurs with peroxide of manganese, chromic acid, and permanganic acid. The oxides of silver, mercury, and gold, are reduced by it to the metallic state under similar conditions.

Distinguishing Tests.—Liberates iodine from iodide of potassium. If peroxide of hydrogen is added to a solution of chromic acid, and the mixture is shaken up with ether, the latter, after separation, assumes a beautiful blue coloration, due probably to the production of perchromic acid.

Physiological Action.—Locally applied, it whitens the skin and acts as a moderate caustic. It is a powerful antiseptic and disinfectant. Internally it produces oxidising and stimulating effects, and in large doses acts as an irritant.

Preparation.—1. By acting on barium peroxide with dilute sulphuric acid—

Barium Peroxide.		Sulphuric Acid.		Barium Sulphate.		Peroxide of Hydrogen.
$Ba O_2$	+	$H_2 S O_4$	=	$Ba S O_4$	+	$H_2 O_2$.

2. By the action of carbonic anhydride on barium peroxide in the presence of water.

If a brisk stream of carbonic anhydride is passed through water to which barium peroxide is added from time to time, peroxide of hydrogen is formed and goes into solution, barium carbonate being precipitated.

Barium Peroxide.		Water.		Carbonic Anhydride.		Barium Carbonate.		Peroxide of Hydrogen.
$Ba O_2$	+	$H_2 O$	+	$C O_2$	=	$Ba CO_3$	+	$H_2 O_2$

Other Modes of Production.—During many processes of oxidation in the presence of water at a comparatively low temperature; for example, the oxidation of phosphorus or of oil of turpentine, in which ozone is simultaneously produced.

NITROGEN.

(*Nitrum, saltpetre, and,* γεννάω, *I produce*) $N = 14$; $N_2 = 28$. *Gas at ordinary temperatures; liquid at* −195° *under a pressure of* 1 *atmosphere, or at* −146° *under* 35 *atmospheres pressure (critical temperature and pressure), the liquid solidifies partially when allowed to evaporate suddenly. Specific gravity of gas* 0·971 (*air*=1); 14 (*H*=1); *of liquid at* −195° 0·885 (*water*=1). *Pentad.* 11·19 *litres weigh* 14 *grammes.*

Occurrence in Nature.—Nitrogen constitutes nearly four-fifths of the bulk of the atmosphere. It is also found abundantly and widely diffused in combination with a few other elements, as in ammonia, in nitrates, or in carbon compounds of complex composition, in the air, in water, in soils, in blood, in all animal tissue, in plants, and in some nebulæ.

Physical Properties.—Nitrogen is a colourless, tasteless, and odourless gas which, like oxygen and hydrogen, was considered to be *permanent* or incondensible until 1877, when it was condensed to a liquid under the conditions above mentioned. Like oxygen and hydrogen (which is least compressible), it follows Boyle's law for moderately high pressures only, becoming at first more compressible as the pressure increases, but gradually diminishing again, and finally becoming less compressible. Thus, under a pressure of 2,790 atmospheres, it is only diminished to $\frac{1}{752}$ of its volume at 1 atmosphere. It is slightly soluble in water, but less so than oxygen. 100 volumes of water absorb 2·03 volumes at 0°, and 1·48 at 15° (Bunsen); or, at the temperature t, and a pressure of 760 mm., if C = its coefficient of solubility, then

$$C = 0{\cdot}020246 - 0{\cdot}00053867\,t + 0{\cdot}00001156\,t^2$$

Its coefficient of expansion is ·003668. Its specific heat = 0·2434 under constant pressure (Regnault). Its absolute index of refraction = 1·00030.

Chemical Properties.—Nitrogen is neither a combustible nor a supporter of combustion (see p. 89), and offers a marked contrast to all other elements in its weak powers of combination. The formation of its compounds can, with few exceptions, only be brought about indirectly, and is attended with *absorption* instead of evolution of heat (Berthelot).

With boron, magnesium, silicon, chromium, and titanium, however, it enters into direct combination at a high temperature. These compounds are termed nitrides.

Hence, it is often termed an *inert* gas, and its properties are aptly described as *negative*. Its compounds are, notwithstanding, numerous, and many are of vast importance, but all are characterised by a greater or less degree of instability.

Thus, with hydrogen, it forms a most powerful base, ammonia ($N H_3$), and the hydrocarbon derivatives of this compound, the so-called organic ammonias, constitute the numerous vegetable alkaloids (quinine, morphia, strychnine, aconitine, thëin, caffëin, piperin, &c.). In direct combination with carbon, it gives rise to an important series of compounds termed cyanides, and among these to prussic acid ($H C N$). It is a constituent also of one of the most powerful acids—viz., nitric acid ($H N O_3$).

Distinguishing Tests.—Nitrogen may be distinguished from all other substances as a colourless, tasteless, and odourless gas, which is neither inflammable nor a supporter of combustion, and which is not absorbed by a solution of potassium or sodium hydrate, and does not turn lime-water milky. These two last negative reactions serve to distinguish it specially from carbonic anhydride.

Physiological Action.—Nitrogen is not poisonous, but is not respirable unless mixed with oxygen. In atmospheric air it plays an important part as a diluent of the oxygen, whose intense activity is considerably diminished by the presence of this inert gas in such large quantity.

Preparation—1. *From Air.*—Nitrogen may easily be obtained from air by the removal of oxygen. If air, which has first been passed through a U-tube containing caustic potash to absorb the carbonic anhydride, be next made to pass through a U-tube containing calcium chloride or pumice-stone moistened with sulphuric acid, to deprive it of its moisture, and is finally allowed to stream slowly through a strong glass tube containing copper turnings or clippings heated to redness in a suitable furnace, the copper combines with the oxygen to form cupric oxide, and pure nitrogen passes on.

$$\begin{array}{ccccccccc} \text{Nitrogen.} & & \text{Oxygen.} & & \text{Copper.} & & \text{Cupric Oxide.} & & \text{Nitrogen.} \\ x\,N & + & O & + & Cu & = & Cu\,O & + & x\,N. \end{array}$$

If the air is mixed with a little ammonia previous to its passage over the heated copper, a small quantity of the latter will suffice for the preparation of any quantity of nitrogen. In this case the copper oxidised by the oxygen is reduced again to the metallic condition by the ammonia; in fact, the oxygen of the air is transferred to the hydrogen of the ammonia, water and nitrogen being the result.

$$\begin{array}{ccccccccc} \text{Ammonia.} & & \text{Cupric Oxide.} & & \text{Copper.} & & \text{Water.} & & \text{Nitrogen.} \\ 2\,NH_3 & + & 3\,Cu\,O & = & Cu_3 & + & 3\,H_2O & + & N_2. \end{array}$$

Many other substances will abstract oxygen from the air more or less rapidly at ordinary temperatures, such as phosphorus (see air, p. 143), moist iron filings, ferrous and manganous oxides, an alkaline solution of pyrogallic acid, &c.; but the above method is the most practical and convenient for the preparation of nitrogen from this source.

2. *From Ammonium Nitrite.*—Very pure nitrogen may be obtained by heating a concentrated solution of ammonium nitrite. The salt breaks up at a temperature a little below the boiling point of the solution into nitrogen and water, thus—

$$\begin{array}{ccccc} \text{Ammonium Nitrite.} & & \text{Water.} & & \text{Nitrogen.} \\ NH_4\,NO_2 & = & 2\,H_2O & + & N_2. \end{array}$$

Or, if to a concentrated solution of potassium nitrite solid ammonium chloride be added, ammonium nitrite and potassium chloride are formed, thus—

$$\begin{array}{ccccccc} \text{Potassium Nitrite.} & & \text{Ammonium Chloride.} & & \text{Ammonium Nitrite.} & & \text{Potassium Chloride.} \\ K\,NO_2 & + & NH_4Cl & = & NH_4\,NO_2 & + & K\,Cl \end{array}$$

And the former salt decomposes on heating, as above described, the potassium chloride remaining unchanged.

3. *By the action of Chlorine on excess of Ammonia.*—If a stream of chlorine be passed through a wash-bottle containing a somewhat concentrated solution of ammonia gas, the ammonia gives up its hydrogen to the chlorine, and nitrogen is copiously evolved, thus—

$$\begin{array}{ccccccc} \text{Ammonia.} & & \text{Chlorine.} & & \text{Hydrochloric Acid.} & & \text{Nitrogen.} \\ 2NH_3 & + & 3Cl_2 & = & 6HCl & + & N_2. \end{array}$$

If the ammonia solution is very concentrated the decomposition is attended with slight explosions and flashes of light.

Caution.—The utmost care must be taken that the ammonia is *in excess*, since when this is not the case chloride of nitrogen is formed by the further action of the chlorine on the resulting ammonium chloride, thus—

$$\begin{array}{ccccccc} \text{Ammonium Chloride.} & & \text{Chlorine.} & & \text{Hydrochloric Acid.} & & \text{Nitrogen Chloride.} \\ NH_4Cl & + & 3Cl_2 & = & 4HCl & + & NCl_3; \end{array}$$

and may give rise to a highly dangerous explosion.

NITRIC ANHYDRIDE.*

(*Nitric pentoxide*) $N_2O_5 = 108$. $[(NO_2)'_2O]$. *Percentage composition*, $N = 25{\cdot}9$; $O = 74{\cdot}1$. *Solid at ordinary temperatures; melting point*, 30°; *boiling point*, 45° *to* 50°. *Specific gravity*, 2·257 (*water* = 1).

Physical Properties.—Nitric anhydride is a colourless, transparent, crystalline solid (rhombic prisms). It is soluble in water with much heat, and the solution is a chemical one, nitric acid being formed.

Chemical Properties.—Nitric anhydride is an acid-forming oxide. It is a very unstable compound, decomposing spontaneously if kept for any length of time. It is highly hygroscopic, and combines with water with much heat, forming nitric acid.

$$\begin{array}{ccccc} \text{Nitric Anhydride.} & & \text{Water.} & & \text{Nitric Acid.} \\ N_2O_5 & + & H_2O & = & 2HNO_3. \end{array}$$

If heated much above 45° it splits up into nitric peroxide and oxygen.

$$2N_2O_5 = 2N_2O_4 + O_2.$$

It is absorbed by nitric acid, and forms with it a crystalline compound, having the composition $2(HNO_3).N_2O_5$.

Preparation—1. *From dry Silver Nitrate by the action of dry Chlorine.*—If dry chlorine is passed over dry silver nitrate at a gentle heat, nitric

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* Nitrogen and oxygen unite with one another in five different proportions (see p. 56).

anhydride is formed, and passes on in the form of vapour, which may be condensed and solidified by means of a freezing mixture, according to the equation—

$$\overset{\text{Argentic Nitrate.}}{2AgNO_3} + \overset{\text{Chlorine.}}{Cl_2} = \overset{\text{Argentic Chloride.}}{2AgCl} + \overset{\text{Nitric Anhydride.}}{N_2O_5} + \overset{\text{Oxygen.}}{O.}$$

2. By mixing at a low temperature phosphoric anhydride and nitric acid, and distilling the mixture at a gentle heat.

3. By the action of nitryl chloride on nitrate of silver—

$$\overset{\text{Argentic Nitrate.}}{AgNO_3} + \overset{\text{Nitryl Chloride.}}{NO_2Cl} = \overset{\text{Nitric Anhydride.}}{N_2O_5} + \overset{\text{Silver Chloride.}}{AgCl.}$$

NITRIC ACID.

(Hydric nitrate, Aqua fortis) $HNO_3 = 63$. $[HO.NO_2]$. *Percentage composition,* $H = 1{\cdot}6$; $N = 22{\cdot}2$; $O = 76{\cdot}2$. *Liquid at ordinary temperatures; boiling point,* 84·5; *freezing point* − 50°. *Specific gravity,* 1·517 (*water* = 1).

Occurrence in Nature.—Nitric acid does not occur free in nature, but is widely distributed in combination with ammonium, potassium, sodium, calcium, and magnesium. As ammonium nitrate it occurs in the air, its formation being due to various causes, among which may be mentioned the passage of electricity in moist air. As potassium nitrate (saltpetre) it occurs as an efflorescence on the soil in India, and as sodium nitrate (Chili saltpetre) in the north of Peru, especially where there is little or no rain. It occurs also in combination in meteorites, and in plants, which latter extract it from the soil.

Physical Properties.—Nitric acid when pure is a colourless, limpid liquid, but is not unfrequently yellow, owing to the presence of oxides of nitrogen in solution. It has a characteristic pungent odour. It is exceedingly hygroscopic, fumes in contact with air, and is miscible in all proportions with water with considerable evolution of heat. The boiling point of such mixtures rises with increasing dilution.

The behaviour of diluted nitric acid to distillation is somewhat remarkable; if containing only a small proportion of water, a comparatively strong acid distils over, and dilute acid remains in the retort. If mixed with a large proportion of water, very dilute acid distils over. The temperature gradually rises to 120·5° at $735^{\text{mm.}}$ bar., and remains stationary at this point, at which an acid containing 32 per cent.

of its weight of water distils over. This is, however, no new hydrate, as its composition varies with the pressure (Roscoe). In other words, both strong and diluted acid are brought by continuous boiling to the same strength (about 68 per cent. acid), subject to slight alteration, according to the atmospheric pressure, and it is only acid of this strength which is capable of distillation without change.

Nitric acid obtained in manufacture has a specific gravity of from 1·2 to 1·5. If this is distilled with strong sulphuric acid, and air is blown through the distillate to remove nitrous acid, pure colourless acid, of composition $HO \cdot NO_2$ is obtained of specific gravity 1·517 at 15·5°, and boiling at 86°, with partial decomposition.

Chemical Properties.—Nitric acid is essentially a monobasic acid, and forms a large and important series of salts called nitrates.

Owing to the readiness with which it parts with its oxygen, it is an extremely active substance and a most powerful oxidising agent. Thus, it converts ferrous into ferric salts, lead sulphide into lead sulphate, liberates iodine from potassium iodide, chlorine from hydrochloric acid, &c. It attacks all organic tissues, and hence all animal and vegetable fabrics.

Exposed to light, it is decomposed with formation of nitric peroxide, and becomes yellow. The reaction may be approximately expressed as follows :—

$$\begin{array}{ccccccc} \text{Nitric Acid.} & & \text{Nitric Peroxide.} & & \text{Water.} & & \text{Oxygen.} \\ 2HNO_3 & = & 2NO_2 & + & H_2O & + & O. \end{array}$$

Even at moderate heat it is decomposed, but at a bright red heat its molecule undergoes complete disintegration, thus :—

$$\begin{array}{ccccccc} \text{Nitric Acid.} & & \text{Nitrogen.} & & \text{Water.} & & \text{Oxygen.} \\ 2HNO_3 & = & 2N & + & H_2O & + & 5O. \end{array}$$

It absorbs nitric oxide, the solution assuming a different colour, according to the specific gravity of the acid; thus, acid of specific gravity 1·25 becomes blue, of specific gravity 1·35 green, of specific gravity 1·45 yellow, and of specific gravity 1·5 red. In acid of specific gravity 1·15 nitric oxide produces no change of colour.

It will be well to consider some of its reactions separately:—

Action on non-Metals.—All non-metals (including arsenic), with the exception of oxygen, hydrogen, nitrogen, fluorine, and chlorine, are converted into their highest oxides when heated with nitric acid, the acid suffering greater or less reduction.

Action on Metals.—This varies according to the strength of the acid and the metal acted on. Gold and platinum and its allied metals, are not acted on by nitric acid of any strength. *Strong acid* has no action on iron, tin, or aluminium, converts antimony and tungsten into insoluble oxides, and dissolves all the other metals, with formation of a nitrate. *Moderately strong acid* dissolves iron, converts tin into insoluble oxide, and acts on the other metals as above. *Diluted acid* dissolves tin with evolution of laughing gas, and acts on many of the metals, such as copper, mercury, silver, only at higher temperatures.

All these reactions are accompanied by a greater or less reduction of the acid, and with the formation of the various lower oxides of nitrogen, and even of ammonia, the following examples are typical:—

1. With carbon the strong acid furnishes *peroxide of nitrogen.*

2. Silver, in the presence of an excess of dilute nitric acid, forms *nitrous anhydride*, which dissolves, forming nitrous acid, thus:—

Silver.		Nitric Acid.		Nitrous Acid.		Argentic Nitrate.		Water.
Ag_2	+	$3HNO_3$	=	HNO_2	+	$2AgNO_3$	+	H_2O.

3. The action of copper on acid of specific gravity 1·25 (see p. 121) furnishes a mode of preparing *nitric oxide*, thus:—

Copper.		Nitric Acid.		Nitric Oxide.		Cupric Nitrate.		Water.
$3Cu$	+	$8HNO_3$	=	$2NO$	+	$3Cu2NO_3$	+	$4H_2O$.

4. Zinc, with dilute nitric acid, yields *nitrous oxide*, thus:—

Zinc.		Nitric Acid.		Nitrous Oxide.		Zinc Nitrate.		Water.
$4Zn$	+	$10HNO_3$	=	N_2O	+	$4Zn2NO_3$	+	$5H_2O$.

5. Zinc or tin, with a somewhat stronger acid, may also give rise to the production of *ammonia*, which combines with the excess of acid, thus—

Zinc.		Nitric Acid.		Ammonia.		Zinc Nitrate.		Water.
$4Zn$	+	$9HNO_3$	=	H_3N	+	$4Zn2NO_3$	+	$3H_2O$.

Action on Organic Matter.—In some cases the action of nitric acid (particularly of the strong acid) on carbon compounds is exceedingly violent and destructive—thus, oil of turpentine is ignited and decomposed by it. In other cases the action is simply an oxidation, as in the conversion of indigotine (C_8H_5NO) into isatin ($C_8H_5NO_2$); in other cases, some of the elements of the acid enter into the molecule of the compound acted upon, the group NO_2 being substituted for hydrogen, as in the conversion of carbolic acid (C_6H_6O) into picric acid $[C_6H_3(NO_2)_3O]$, or a nitric ether is formed, as in the conversion of glycerine ($C_3H_8O_3$) into nitro-glycerine $[C_3H_5(NO_3)_3]$, or of cotton ($C_6H_{10}O_5$) into gun-cotton $[C_6H_7O_2(NO_3)_3]$.

Distinguishing Tests.—Nitric acid, when free, may be distinguished as a colourless or yellowish liquid which fumes strongly in air, and yields red fumes when brought into contact with copper, and which stains the skin yellow.

Nitrates may be recognised as follows:—

If to a cold solution containing a nitrate a cold solution of ferrous sulphate be added in a test tube, and strong sulphuric acid is carefully poured in so as to form a layer at the bottom of the tube, nitric oxide is evolved, and, dissolving in the ferrous sulphate solution, causes an amethyst or brown-coloured ring to be formed at the point where the liquids meet.

Physiological Action.—Its vapour produces spasmodic cough and violent inflammation of the lungs when inhaled. It blisters and destroys the skin, staining it yellow. It is a violent, corrosive poison.

Preparation—1. *From Nitrate of Potassium by the action of Sulphuric Acid.*—Powdered potassium nitrate is placed in a retort with about an equal weight of strong sulphuric acid. On heating moderately upon a sand-bath or over wire-gauze, the nitrate is decomposed, acid sulphate of potassium (hydric potassic sulphate) being formed and nitric acid distils over. The vapours may be condensed in a suitable receiver by cooling. The decomposition may be expressed as follows:—

Potassium Nitrate.		Sulphuric Acid.		Hydric Potassic Sulphate.		Nitric Acid.
KNO_3	+	H_2SO_4	=	$KHSO_4$	+	HNO_3.

Manufacture.—In the manufacture of nitric acid, sodium nitrate, as the cheaper salt, is generally used, and only half the proportion of sulphuric acid. Neutral sulphate of sodium is thus produced, but the process requires a much higher temperature, and may be considered to take place in two stages:—

Sodic Nitrate.		Sulphuric Acid.		Sodic Hydric Sulphate.		Nitric Acid.		Sodic Nitrate.
$2NaNO_3$	+	H_2SO_4	=	$NaHSO_4$	+	HNO_3	+	$NaNO_3$.

In the second stage, at the higher temperature the undecomposed sodium nitrate and the acid sulphate react upon one another, thus:—

Sodic Nitrate.		Sodic Hydric Sulphate.		Sodic Sulphate.		Nitric Acid.
$NaNO_3$	+	$NaHSO_4$	=	Na_2SO_4	+	HNO_3.

Other Modes of Production.—1. By the passage of electric sparks through moist air, together with nitric peroxide. 2. By the decay and oxidation of nitrogenised organic matter, in presence of alkalies and of a special kind of bacterium (nitrate bacterium). By these means nitrogenised organic matters are destroyed and converted into innocuous compounds; hence, the presence of nitrites and nitrates in our soils and well waters. 3. When a mixed jet of hydrogen and nitrogen is burnt in air. 4. By the oxidation of ammonia.

Fuming Nitric Acid.—This is a name given to a highly-concentrated form of the acid, a portion of which has undergone decomposition in distillation at a higher temperature than 120°, and which contains, therefore, nitric peroxide in solution. The presence of the nitric peroxide (*q.v.*) increases its oxidising powers, and imparts to it a deep yellow colour, and causes it to emit dense red fumes.

Applications.—In anilin factories, in the manufacture of sulphuric acid, picric acid, nitro-glycerine, and gun-cotton, in the separation of silver from gold, &c., &c.

NITROUS OXIDE.

(*Nitrogen monoxide, laughing gas*) $N_2O = 44$. *Percentage composition*, $O = 36{\cdot}23$, $N = 63{\cdot}77$. *Gas at ordinary temperatures; liquid at* 0° *under* 30 *atmospheres pressure; boiling point of liquid* $-92°$; *freezing point* $-99°$. *Specific gravity of gas*, 1·527 (*air*=1); 22 (*H*=1); *of liquid*, 0·90 (*water*=1). 11·19 *litres of the gas weigh* 22 *grammes.*

Physical Properties.—Nitrous oxide is a colourless gas, possessing a peculiar sweetish taste and smell. At 7·2° it requires a pressure of 50 atmospheres, at 0°, of 30 atmospheres for its liquefaction. In the liquid form it is colourless and lighter than water, and, if allowed to expand suddenly, may be frozen to a white crystalline solid, which (unlike solid carbonic anhydride) melts in contact with the skin, producing a blister. The liquid may also be frozen by blowing air through it. If liquid nitrous oxide is mixed with bisulphide of carbon, a temperature of $-140°$ may be produced when the mixture is evaporated under the receiver of an air-pump. The gas is somewhat soluble in cold water, 1 volume of water absorbing about 1 volume of the gas, but is less soluble in a saline solution. Alcohol also absorbs it.

Chemical Properties.—Nitrous oxide is a neutral oxide. The gas bears in its chemical properties so striking a resemblance to oxygen that it might possibly be mistaken for that gas. Thus, it is not inflammable, but ignites a glowing splint and supports the combustion of many substances, such as charcoal, sulphur, phosphorus, magnesium, iron, &c., which burn in it with a brilliancy scarcely inferior to that produced by their combustion in oxygen. Red fumes (due to higher oxides of nitrogen) are, however, generally formed. Exploded with an equal volume of hydrogen, an equal volume of nitrogen is left after the explosion. If passed through a red-hot porcelain tube it is decomposed into nitrogen and oxygen. It may also be deprived of its oxygen by passage over oxidisable substances, and under these circumstances yields its own volume of nitrogen.

Distinguishing Tests.—A colourless gas resembling oxygen in many respects, but distinguished from that gas by its greater specific gravity, its sweet smell and taste, its far greater solubility in water, and by its not forming red fumes with nitric oxide.

Physiological Action.—The gas owes its trivial name to its remarkable intoxicating and exhilarating effect when inhaled, mixed with air. If taken into the lungs, unmixed with atmospheric air, it rapidly produces insensibility, without, however, the unpleasant after-effects of other anæsthetics. It has been much used of late years in dentistry; when the inhalation of the gas is discontinued, the patient rapidly recovers from the effects, but when such recovery, or partial recovery, has taken place, it is not without danger to subject the patient again to the influence of the gas unless an interval of at least several hours has elapsed.

Preparation—1. *From Ammonium Nitrate.*—By gently heating fused ammonium nitrate in a retort this salt splits up into nitrous oxide and water. The gas must be collected over hot water, owing to its solubility in cold, or over a strong brine. The reaction may be expressed as follows:—

Ammonium Nitrate.		Nitrous Oxide.		Water.
NH_4NO_3	$=$	N_2O	$+$	$2H_2O$.

If the salt is heated too strongly, the nitrous oxide may be decomposed into its elementary constituents with explosion, or higher oxides of nitrogen may be evolved.

If the gas is to be used for inhalation, great care should be taken to have the nitrate of ammonia employed free from chloride of ammonium, otherwise the gas will be contaminated with chlorine. The gas may be purified by passing it over hydrate of lime.

NITRIC OXIDE.

(*Nitrogen dioxide*) $NO = 30$.* *Percentage composition,* $N = 46{\cdot}67$; $O = 53{\cdot}33$. *Gas at ordinary temperatures; liquid at* $-11°$ *under* 104 *atmospheres pressure. Specific gravity,* 1·039 (*air* = 1); 15 (*H* = 1). 11·19 *litres weigh* 15 *grammes. Boiling point* – 153°·6.

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* Nitric oxide forms one of the very few exceptions to the rule that the valency of an element changes, if it changes at all, by two or a multiple of two. Nitrogen is generally a

Physical Properties.—Nitric oxide is a colourless gas which can be condensed under the conditions above given. It is impossible to say whether the gas possesses any taste or smell, since it unites with the oxygen of the air by mere contact with it, forming red fumes of nitric peroxide and nitrous anhydride. It is but very slightly soluble in water. It is absorbed by a solution of ferrous sulphate, with a deep brown coloration, being expelled from this solution unaltered on boiling.

Chemical Properties.—Nitric oxide is specially characterised by its attraction for oxygen, forming deep red fumes of nitric peroxide and nitrous anhydride by mere contact with air. This reaction serves as a means of detecting oxygen in a mixture of gases. Like nitrous oxide, it will not burn, but supports the combustion of certain elements, if these are strongly ignited beforehand. Thus, a taper plunged into the gas is put out, but phosphorus, charcoal, sulphur, magnesium, and iron will burn brilliantly in it, red fumes of higher oxides of nitrogen being formed. Its action on nitric acid of different specific gravities has already been alluded to (see nitric acid, p. 116). It combines also with chlorine and bromine.

The quantity of heat disengaged by the combustion of elements in nitric oxide is greater than that produced by their combination with oxygen, the combustion of nitrogen and oxygen being endothermic (p. 72).

Nitric oxide saturated with the vapour of bisulphide of carbon produces an inflammable, or very feebly explosive mixture, which, when ignited, yields one of the most intensely brilliant and chemically active of luminous flames.

Distinguishing Tests.—Nitric oxide may be distinguished from all other gases, as a colourless gas, which forms red fumes in contact with air or oxygen. When heated with metallic sodium, a volume of nitrogen equal to half the volume of the nitric oxide is left behind.

Preparation—*From Nitric Acid by the action of Copper.*—The nitric acid employed should have a specific gravity between 1·2 and 1·3, and may then be poured upon the copper in a flask similar to that used in the preparation of hydrogen. If the acid is of this strength, the reaction goes on regularly and without violence. Red fumes are at first formed in the flask, but when all the air has been expelled, the

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perissad, but in nitric oxide it is an artiad (p. 6[illegible]). This difficulty cannot be overcome by doubling the formula for all the properties of the gas, its permanence, compared to nitrous oxide, its greater stability generally, as well as its specific gravity, all render the formula N O imperative.

gas remains colourless. It may be collected in the usual manner by displacement of water. The reaction may be expressed as follows:

$$\overset{\text{Copper.}}{3\,Cu} + \overset{\text{Nitric Acid.}}{8\,H\,N\,O_3} = \overset{\text{Cupric Nitrate.}}{3\,Cu\,2\,N\,O_3} + \overset{\text{Water.}}{4\,H_2\,O} + \overset{\text{Nitric Oxide.}}{2\,N\,O.}$$

2. *By the action of silver or of mercury on nitric acid.* 3. *By heating potassium nitrate with a solution of ferrous chloride in excess of hydrochloric acid.* $6\,Fe\,Cl_2 + 2\,K\,N\,O_3 + 8\,H\,Cl = 3\,Fe_2\,Cl_6 + 2\,K\,Cl + 4\,H_2\,O + 2\,N\,O.$

NITROUS ANHYDRIDE.

(Nitrogen trioxide) $N_2\,O_3 = 76$. *Gas at ordinary temperatures. Percentage composition,* $N = 36{\cdot}84$; $O = 63{\cdot}16$.

Owing to the unstable character of this compound it is impossible to give more than an approximate account of its properties.

Physical Properties.—When free from nitric peroxide it appears to be an indigo blue liquid, boiling at 2°, which does not freeze at − 30°, but when mixed with nitric peroxide its boiling point rises from 2° to 22°. It gives off deep red fumes which are easily condensed by passage through a U-tube surrounded by a freezing mixture. It dissolves in water below 0° with a blue colour, but above that temperature is decomposed by water.

Chemical Properties. — Nitrogen trioxide is an acid-forming oxide whose hydrate has the formula, $H\,N\,O_2$ (*nitrous acid*), and a large series of salts are known, whose composition correspond to this hydrate, although the hydrate itself can scarcely be said to be known except in solution. In the presence of a small quantity of water (at a low temperature) nitrous acid is formed—$N_2\,O_3 + H_2\,O = 2\,H\,N\,O_2$. In the presence of an excess of water it forms nitric acid and nitric oxide—$3\,N_2\,O_3 + H_2\,O = 4\,N\,O + 2\,H\,N\,O_3$. If the vapours of nitrogen trioxide are passed into a solution of potassium or sodium hydrate, potassium or sodium nitrite is formed—$2\,K\,H\,O + N_2\,O_3 = 2\,K\,N\,O_2 + H_2\,O$.

Distinguishing Tests.—A deep red gas, condensible by cold, and yielding nitrous acid when mixed with a little cold water.

Physiological Action.—Highly irritating gas readily producing inflammation of the lungs (see also p. 125).

Preparation— 1. *By mixing Nitric Oxide and Oxygen.* — If four volumes of nitric oxide are mixed with one volume of oxygen, nitrous anhydride results, according to the equation—

$$4NO + O_2 = 2N_2O_3.$$

2. *By heating Nitric Acid with Arsenious Acid.* — If nitric acid of specific gravity 1·33 is heated with arsenious acid, red fumes are given off in abundance, which are a mixture of nitric peroxide and nitrous anhydride.

The fumes may be condensed in a cooled receiver, and nitric oxide passed through the liquid so obtained, and the fumes once more condensed by means of a freezing mixture. In this way comparatively pure nitrous anhydride is obtained.

3. *By heating nitric acid (of specific gravity* 1·25) *with starch.*

NITROUS ACID.

$HNO_2 = 47$—*Percentage composition*, $H = 2{\cdot}13$, $N = 29{\cdot}79$, $O = 68{\cdot}08$.

Occurrence in Nature.—Nitrous acid occurs in the atmosphere in combination with ammonia as ammonium nitrite (see ammonia), and in well waters, contaminated by sewage. It is found accompanying nitrates in rain and in the soil; in the latter, probably, owing to the action of a specific bacterium or nitrogenised organic matter in presence of alkalies.

Physical Properties.—A blue solution.

Chemical Properties.—The pure acid is unknown, and even its solution is very unstable, being decomposed when slightly heated, with formation of nitric acid, nitric oxide, and water.

$$\underset{\text{Nitrous Acid.}}{3HNO_2} = \underset{\text{Nitric Acid.}}{HNO_3} + \underset{\text{Nitric Oxide.}}{2NO} + \underset{\text{Water.}}{H_2O.}$$

It forms, however, a considerable series of more or less stable salts called nitrites.

Its most striking characteristic is that, according to circumstances, it may act either as a powerful oxidising, or else as a reducing agent, being with equal facility reduced to nitric oxide on the one hand, or oxidised into nitric acid on the other. Thus, it liberates iodine from iodide of potassium by oxidation, and rapidly decolourizes a solution of permanganate of potassium by reduction.

Distinguishing Tests.—Nitrous acid in combination (nitrites) may be detected by the addition of **cold** dilute sulphuric acid, and of ferrous sulphate solution which becomes brown by absorption of the nitric oxide formed (distinction from nitrates). Warmed with dilute sulphuric acid, nitrites give off reddish brown fumes.

If to a solution of a nitrite, iodide of potassium be added and a solution of starch, on making the solution acid with acetic acid an intense blue colour is produced. Solutions of a nitrite, after being acidified with sulphuric acid, give a yellow or brown colour with a solution of meta-diamido-benzol.

Physiological Action.—Exerts a powerful effect on the heart's action, and in the form of an alkaline nitrite is very poisonous in doses of even a few grains.

Preparation.—Owing to the instability of the acid, it is almost impossible to prepare it in the free state. A comparatively stable solution of it may be obtained by mixing liquid nitrous anhydride with a little water at a low temperature, but this is decomposed on boiling.

Preparation of Nitrites.—1. By heating nitrates alone or with reducing agents.*

NITRIC PEROXIDE.

(*Tetroxide of Nitrogen, Nitryl*) $N_2O_4 = 92$. ($NO_2 = 46$.) *Percentage composition*, $N = 30{\cdot}44$, $O = 69{\cdot}56$. *Gas at higher temperatures; liquid at lower temperatures; solid at* −20°. *Specific gravity of liquid*, 1·451 (*water* = 1).

Physical Properties.—Nitric peroxide is a vapour of an intense brown-red colour, of somewhat sweet and very pungent odour and acid taste, which, when cooled to a very low temperature by means of a freezing mixture, becomes liquefied, and, in the absence of all moisture, solidified to a crystalline solid. The crystals are said to melt at −9°, and, when once melted, do not again solidify till −20° or even −30°. Slightly above −9° the liquid is said to be almost colourless; but, as the temperature rises, the colour changes from light to orange yellow; at 22° the liquid boils, giving off a dense vapour of a brown-red colour, which at 40° becomes almost black, its specific gravity decreasing as the temperature rises, until at from 150° to 180° its density is diminished by nearly one-half, pointing clearly to the dissociation of the molecule, N_2O_4, into two

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* Nitrites are best prepared pure by double decomposition of silver nitrite obtained by heating potassium nitrate for some time to fusion, dissolving the fused mass in a little water and adding a solution of nitrate of silver; silver nitrite is precipitated, and may be collected, washed with a little water, and dried over oil of vitriol.

molecules of the composition, NO_2. It has a remarkable selective absorbing power on white light, producing a spectrum crossed along its whole length by many fine absorption lines. It is soluble in nitric acid in considerable quantities.

Chemical Properties.—The dense red fumes which are formed when nitric oxide comes into contact with air or oxygen, consist of nitric peroxide, or of a mixture of nitric peroxide and nitric anhydride, according to the quantity of oxygen involved in the reaction.

It was formerly considered to be an anhydride, since it appears to form salts with certain oxides; thus, with lead monoxide, it apparently forms the compound PbO, N_2O_4, or so-called lead "hyponitrite," and was itself at one time called "hyponitric acid." This lead "hyponitrite" is, however, a double salt of lead nitrate and nitrite, thus:—

Lead "Hyponitrite."		Lead Nitrate.		Lead Nitrite.
$2\,PbO\,N_2O_4$	$=$	$Pb(NO_3)_2$	$+$	$Pb(NO_2)_2$.

Mixed with a small proportion of water it yields nitrous anhydride and nitric acid, thus:—

$$2\,N_2O_4 \quad + \quad H_2O \quad = \quad N_2O_3 \quad + \quad 2\,HNO_3.$$

With a larger quantity of water it yields at first nitric and nitrous acids, but finally nitric acid and nitric oxide, thus:—

$$N_2O_4 \quad + \quad H_2O \quad = \quad HNO_3 \quad + \quad HNO_2.$$
$$3\,HNO_2 \quad = \quad H_2O \quad + \quad HNO_3 \quad + \quad 2\,NO.$$

It is a very powerful oxidising agent. When absorbed by nitric acid it imparts a still greater power of oxidation to it (acid nit. fumans, p. 119).

Carbon and phosphorus will burn in its vapour, but sulphur only with difficulty. With chlorine it unites directly, forming a compound of composition, NO_2Cl (nitric chlorodioxide, nitryl chloride).

Its atom or half molecule, NO_2, acts as a univalent radical (p. 78), and is capable of substituting hydrogen, in many substances yielding a class of compounds known as nitro-compounds (see nitric acid).

Distinguishing Tests.—Concentrated solutions of the alkalies convert it into a mixture of nitrate and nitrite; dilute solutions yield chiefly nitrate with evolution of nitric oxide.

Physiological Action.—Powerful irritant, producing, when inhaled, serious congestion and inflammation of the lungs. Its action, like that of nitrous anhydride, being remarkable on account of the apparent disappearance of the dangerous symptoms for a time, which, however, may recur after some hours with increased violence, often resulting in death. The highly dangerous character of the gases produced by burning, or improperly detonated dynamite, gun-cotton, and similar substances, is in great measure due to the production under such conditions of this and the preceding compound.

Preparation—1. *By heating Lead Nitrate.*—If plumbic nitrate be heated in a hard glass tube to a red heat, and the vapours so produced are passed through a U-tube, which is immersed in a freezing mixture, a red liquid is obtained, which, if the receiver be soon changed, will solidify in a crystalline form. Every precaution must be taken to avoid moisture.

$$\overset{\text{Lead Nitrate.}}{Pb(NO_3)_2} = \overset{\text{Nitric Peroxide.}}{N_2O_4} + \overset{\text{Lead Monoxide.}}{PbO} + \overset{\text{Oxygen.}}{O.}$$

2. *By mixing Nitric Oxide with Oxygen.*—If two volumes of nitric oxide are mixed with one volume of oxygen, red fumes of nitric peroxide are formed—

$$2NO + O = N_2O_4;$$

and if the mixed gases are strongly cooled the liquid or solid peroxide may be obtained.

3. *By the decomposition of nitric acid (q.v.)*

AMMONIA.

(*Sal ammoniac, first obtained in Libya, near the Temple of Jupiter Ammon*) $NH_3 = 17$. *Percentage composition*, $H = 17{\cdot}65$; $N = 82{\cdot}35$. *Gas at ordinary temperatures; liquid at* $-40°$, *or at* $0°$ *under* 4·5 *atmospheres pressure; solid at* $-80°$. *Specific gravity*, 0·589 (*air*$=1$); 8·5 ($H=1$); *of liquid*, 0·623 (*water*$=1$). 11·19 *litres weigh* 8·5 *grammes.*

Occurrence in Nature.—Ammonia occurs diffused throughout the atmosphere as ammonium carbonate, nitrite, and nitrate (1 to 40 parts in one million). It is, therefore, always found in rain-water and snow, and since it is one of the products of decomposition by putrefaction or decay of animal or vegetable matters, it also occurs where such decomposition is going on. It is always found in soils, in plants, in the animal body, &c.

Physical Properties.—Ammonia is a colourless gas, having a most peculiar and highly pungent odour, which is by no means unpleasant when the gas is diluted with air. It belongs to the more easily condensible gases, requiring only 6·5 atmospheres pressure at 10° for its liquefaction

Or it may be liquefied by cooling to −40°. It solidifies at −80°.

Liquid ammonia is a mobile fluid of higher refractive power than water. It has a specific gravity of 0·6234 (water = 1). It boils at −33°·7. Subjected to the action of a bath of solid carbonic anhydride and ether, it freezes to a crystalline solid, melting at −75°; or, if evaporated with sulphuric acid, a portion freezes, and sinks through the liquid.

The liquefaction may be brought about in a Faraday tube,* one limb of which contains silver chloride, or calcium chloride, saturated with dry ammonia gas, the other limb being empty, and the whole hermetically sealed. On heating the limb containing the chloride and cooling the other limb, the gas condenses by its own pressure.

Or charcoal may be saturated with the gas in a Faraday tube with the same result. On cooling the tube after an experiment the liquid ammonia is absorbed, and if water is present a crystalline hydrate is often formed, owing to the rapid evaporation and the consequent production of cold.

The solubility of ammonia gas in water is one of its most striking characteristics, and exceeds that of all other gases. One volume of water at 0° absorbs 1,050 volumes of ammonia; at 10°, 813 volumes; at 15°, 727 volumes; at 25°, 586 volumes. A vessel filled with dry ammonia, when opened under water, is filled almost instantaneously, so rapid is the absorption, and when of glass, is very liable to be broken by the violent inrush of the water.

The specific gravity of the solution *decreases as the saturation increases*—thus, at 14° ammonia solution containing 10 per cent. by weight of ammonia has a specific gravity of 0·959; containing 20 per cent. by weight, 0·925; 30 per cent. by weight, 0·897; 36 per cent. by weight, 0·884. A saturated solution at 15·5° contains one-third of its weight of the gas, and occupies one-and-a-half times the original volume of the water from which it was produced. The solution is known as *liquor ammoniæ* (*spirits of hartshorn*), and is a very important reagent in the laboratory. A concentrated solution of the gas freezes at −40° to a jelly-like non-volatile mass, losing its smell almost entirely.

Chemical Properties.—Ammonia belongs to the class of bodies called bases, though, more strictly speaking, it only acts as a base when combined with a molecule of water; thus, it neutralises all acids, forming crystalline salts (isomorphous with potassium salts), but, instead of replacing the hydrogen, it combines with the whole molecule of the acid, *e.g.*:—

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* A tube of strong glass, shaped like an inverted V, so that one limb containing the gas (combined or absorbed) may be heated, and the other, in which the gas is condensed by its own pressure, cooled if necessary.

$$\overset{\text{Ammonia.}}{N H_3} + \overset{\text{Hydrochloric Acid.}}{H Cl} = \overset{\text{Ammonium Chloride.}}{N H_4 Cl}$$

$$\overset{\text{Ammonia.}}{N H_3} + \overset{\text{Nitric Acid.}}{H N O_3} = \overset{\text{Ammonium Nitrate.}}{N H_4 N O_3}$$

$$\overset{\text{Ammonia.}}{2 N H_3} + \overset{\text{Sulphuric Acid.}}{H_2 S O_4} = \overset{\text{Ammonium Sulphate.}}{(N H_4)_2 S O_4}.$$

The compound radical $N H_4$ thus plays the part of a metal; hence, the name *ammonium* has been given to it, and it is frequently represented by the symbol *Am*. Thus, we may write—

$$Am Cl = N H_4 Cl,\ Am N O_3 = N H_4 N O_3,\ Am_2 S O_4 = (N H_4)_2 S O_4;$$

and to complete the analogy with the alkali metals, the hydrate or hydroxide is often written—

$$Am H O = N H_4 H O = N H_3, H_2 O.$$

Ammonia gas is a non-supporter of combustion, and is combustible with difficulty, except at a high temperature; but, when mixed with air or oxygen, it burns with a green flame, yielding water and nitrogen. Mixed with air and passed over heated spongy platinum it combines with oxygen, forming nitric acid.

If passed through a red-hot tube it is decomposed into its elementary constituents, and the same occurs when a series of electric sparks are passed through the gas, its volume under these circumstances becoming doubled. It is also decomposed into its elementary constituents if passed over heated potassium, potassium nitride being formed, and hydrogen passing on. Its decomposition by chlorine with formation of hydrochloric acid and nitrogen has already been referred to (see nitrogen, p. 114).

Distinguishing Tests.—Ammonia may be distinguished from all other substances as a colourless gas, having a remarkably pungent odour, and when moist a powerfully alkaline reaction; extremely soluble in water, the solution being alkaline to test-paper; neutralising all acids, and forming a white cloud with the vapours of all the volatile acids. It is evolved from its combinations with acids by boiling them with a solution of potash or other fixed alkali, and may then be recognised as indicated above.

Physiological Action.—Stimulant and irritant. If breathed undiluted it inflames the bronchial tubes.

Preparation—1. *From ammonium chloride by the action of caustic potash* *or lime.* About equal weights of ammonium chloride and slacked lime are mixed together, and sufficient water added to form a stiff paste. On heating the mixture in a flask upon a sand-bath, ammonia gas is copiously evolved, which, after washing in a small quantity of water, may be collected by upward displacement of air or over mercury. If required dry it must be passed over stick potash (KHO), or quicklime (CaO) in lumps.*

$$\overset{\text{Ammonium Chloride.}}{2NH_4Cl} + \overset{\text{Slacked Lime.}}{CaH_2O_2} = \overset{\text{Calcium Chloride.}}{CaCl_2} + \overset{\text{Ammonia.}}{2NH_3} + \overset{\text{Water.}}{2H_2O};$$

or the gas may be passed into water if the solution is required.

2. It is also readily obtained by gently heating a saturated solution and passing the gas evolved over stick potash.

Other Modes of Production.—3. When a mixed jet of hydrogen and nitrogen is burnt in air, nitrate and nitrite of ammonium are formed. 4. By passage of hydrogen and any lower oxide of nitrogen over platinum sponge at a red-heat. 5. By the action of nascent hydrogen on the oxides of nitrogen. 6. By the decay of nitrogenous matter. 7. By the destructive distillation of nitrogenised matters, particularly in the presence of an excess of a hydroxide of an alkali metal or of lime.

Manufacture.—1. By the destructive distillation of nitrogenised animal matter absorbing the ammonia so produced by acids, and decomposing the resulting ammonium salts by lime.

2. As a bye-product in the manufacture of coal-gas (p. 134).

Carre's Freezing Machine.—Liquid ammonia is obtained on a large scale by heating a concentrated solution of ammonia contained in an iron boiler connected air-tight with an iron condensing vessel, which is kept cool by water; the ammonia expelled from the solution is liquefied in the condenser by its own pressure. If the connection between boiler and condenser is cut off until the water in the boiler is cold, and the stop-cock then opened, the liquid ammonia begins to boil, the gas being reabsorbed by the water in the boiler with production of great cold in the condenser. This alternate process of condensing the ammonia gas, and reabsorbing it in the water in which it was previously dissolved, may be carried on an indefinite number of times, and the apparatus is one of the simplest and most effective ice-producing machines.

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* It enters into combination with sulphuric acid and with calcium chloride, which are the usual substances employed for drying gases.

CARBON.

(Carbo, coal) $C = 12$. *Solid at all temperatures. Specific gravity as diamond,* 3·52, *as graphite,* 2·2 *(water = 1). Tetrad.*

Occurrence in Nature.—Pure carbon occurs in nature under two very distinct forms—viz., as *diamond* in India, Brazil, Borneo, and the Cape; and as *graphite* (plumbago, black-lead) in Cumberland, Ceylon, the United States, China, and S. Siberia. In the less pure form, as the result of the gradual decomposition of vegetable tissue, it forms the numerous and immense deposits of *coal* in various parts of the world. In combination, carbon occurs as an essential constituent of all animal and vegetable matter in its multitudinous variety, and is present in a large class of commonly-occurring minerals known as carbonates. Its compound with oxygen, called carbonic anhydride (CO_2), is a never-failing constituent of the atmosphere (*q.v.*), and is always present either free or in combination in greater or less quantity in natural waters.

Physical Properties of the various Natural and Artificial Forms of Carbon.—This element exhibits the phenomenon of allotropy in a remarkable degree. In considering its physical properties, therefore, it will be necessary to include its many artificial, in addition to its natural, forms, and as these all differ greatly in their physical characteristics they will be best considered separately. All are non-volatile, infusible, and insoluble * in all ordinary solvents.

The specific heat of diamond = 0·1128 at 10°, 0·4589 at 985°; of gas coal = 0·32 at 20°, 0·5 at 2000°; of graphite = 0·1437 at 10°, 0·3250 at 250°, so that at higher temperatures carbon obeys Dulong and Petit's law (p. 32).

A. *Natural Forms.*

1. *Diamond.*—This purest form of the element carbon is found usually in colourless, transparent crystals (octohedra) of the regular system. The surfaces of the crystals are usually convex, and their edges blunt. They are sometimes found coloured yellow, blue, green, rose-red, or dark-brown, owing to the presence of impurities. Its specific gravity varies from 3·5 to 3·55. The diamond is not fusible at any known temperature (air being excluded), but it swells and

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* Animal charcoal disappears when heated with chlorine water, carbonic anhydride being formed, and is similarly oxidised by nitric acid, but these are not genuine solutions of carbon as such.

becomes opaque in the electric arc. It is the hardest substance known, being only approached in this respect by boron. It is not soluble in any medium. It becomes electric by friction, and is a non-conductor of electricity. It is especially characterised by its high refractive power. Its refractive index = 2·47 to 2·75. Its limiting angle* = 23°42′; hence, all the light incident upon it in an arc of 180° is concentrated within an angle of 47°22′. This and its great dispersive power and durability constitute its high value as a gem. Some diamonds absorb light, and become luminous in the dark.

2. *Graphite.*—This slightly less pure form of carbon (known also as plumbago or black-lead) presents an extraordinary contrast to diamond in its physical properties. It is a grayish-black, opaque, solid, crystallising in six-sided plates of the hexagonal system, or appears in amorphous masses of metallic lustre. It is very soft, leaving a black mark when rubbed on paper; hence its familiar application in pencils. Its specific gravity varies from 1·8 to 2·5, according to its purity, but is much less than that of diamond. It is not soluble in any ordinary medium, but is dissolved by molten iron, from which it crystallises on cooling. It is a conductor of electricity. It is infusible, and combustible with great difficulty only, hence its application for crucibles which have to stand very high temperatures.

Coal.—Coal is the result of the gradual decomposition (or, more accurately, of the slow but imperfect combustion) of vegetable matter. It contains, like all vegetable matter, carbon, hydrogen, oxygen, and some nitrogen; but its preponderating constituent is carbon, of which brown coal contains from 60 to 70 per cent., ordinary black coal from 76 to 90 per cent., and anthracite from 94 to 98 per cent. On complete combustion it leaves an ash varying in quantity from 0·5 to 25 per cent., consisting of silicate of alumina, or of calcium sulphate and iron sulphide, together with carbonates of calcium and magnesium, small quantities of chlorides, and a trace of iodides. The specific gravity of coal varies from 1·25 to 1·75.

B. *Artificial Forms.*

Coke.—Coke is the residue after the dry distillation of coal. It is characterised by great porosity and comparative lightness. It is a good conductor of heat and electricity. Its specific gravity varies from 1·6 to 2. It contains on an average from 85 to 92 per cent. of carbon, and from 3 to 5 per cent. of ash.

Wood Charcoal.—This is the residue from the destructive distillation

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* *Limiting Angle.*—The angle beyond which total reflection takes place (p. 43).

of wood, and is also characterised by great porosity and lightness. It usually shows the structure of the wood from which it was obtained. It has the power of absorbing gases in considerable but varying quantity, as will be seen from the following tabular statement:—

ABSORPTIVE POWER OF CHARCOAL FOR GASES (*Saussure*).

GAS.	Volumes absorbed by 1 Volume Boxwood Charcoal
Ammonia, ...	90
Sulphurous anhydride, ...	65
Hydrochloric acid, ...	85
Hydrogen sulphide, ...	55
Nitrous oxide, ...	40
Carbonic anhydride, ...	35
Carbonic oxide, ...	9·4
Oxygen, ...	9·3
Nitrogen, ...	7·5
Hydrogen, ...	1·75

It contains from 60 to 85 per cent. of carbon, according to its method of preparation.

Animal Charcoal.—This is a black, gritty powder obtained by the dry distillation of bones, and consists of about 10 per cent. carbon, 84 per cent. phosphate, and 6 per cent. carbonate of calcium. It has the property of absorbing colouring matters from solution, and even some mineral matters are removed from solutions by it—a property usually supposed to be due to its great porosity. This power is greatly increased by the removal of the calcium phosphate by hydrochloric acid.

Lampblack.—This is a somewhat pure form of finely divided carbon separated from certain hydrocarbons (resins), on incomplete combustion. *Soot* is one of its many forms.

All forms of charcoal have the power, in a greater or less degree, of absorbing gases, and this power is the greater the more finely ground the charcoal is. On this account charcoal acts as a powerful deodorant; it not only absorbs offensive gases, but oxidizes them, burns them up, by virtue of the oxygen also absorbed in its pores. It also has the power of removing many substances from solution, and is largely used in sugar and other manufactories for removing colouring matters from solution. For this purpose animal charcoal is chiefly used.

Chemical Properties of the Element Carbon.—Carbon at somewhat elevated temperatures possesses considerable combining powers, and unites directly with hydrogen, oxygen, sulphur, and with iron and some other metals. Its attraction for oxygen constitutes it a powerful *reducing agent* (p. 85), for which purpose it is used in the laboratory, in the form of charcoal, and in the manufacture of iron and of many other metals from their ores, in the form of coal. It forms only two compounds with oxygen—viz., carbonic anhydride ($C O_2$), and carbonic oxide ($C O$).

Its very varied natural and artificial forms may be proved to consist of one and the same element, from the fact that they all, when burned in oxygen, yield one and the same compound—viz., carbonic anhydride. Diamond fused with potassium nitrate ($K N O_3$) forms carbonate of potassium. When so burnt, diamond leaves a minute trace of ash, showing it to be almost pure carbon, and lampblack, when carefully prepared, approaches the same purity; graphite leaves from 2 to 5 per cent. of ash, and coal from 0·5 to 25 per cent.

1 gramme of carbon when burnt in oxygen evolves 8,000 heat-units.

Carbon, in addition to its power of combining with other elements, has also the power of combining with itself, so that with one and the same element, it is capable of forming an almost infinite series of compounds in which the carbon atoms are linked, as it were, one with the other. In this manner it forms an almost endless series of compounds with hydrogen, called hydrocarbons, and, from each of these, innumerable derivatives may be formed. The facts relating to these hydrocarbons and their derivatives constitute the immense branch of chemical science known as organic chemistry.

Distinguishing Tests.—Carbon may be always distinguished as a black solid (with the usual exception of diamond), infusible and non-volatile, which, when burned in air or oxygen, yields a gas ($C O_2$), specially recognisable by its forming a white precipitate ($Ca C O_3$), with lime water.

Physiological Action.—Animal charcoal has been used as an antidote to vegetable poisons, which it absorbs and renders harmless (Garrod).

Preparation or Manufacture of some forms of Carbon—*Diamond.*—Diamond has not, as yet, been prepared artificially.

Graphite.—1. By dissolving charcoal in fused cast-iron; leaflets of graphite are formed on cooling. 2. By heating diamond in the electric arc.

Vegetable Charcoal.—By heating wood in iron retorts or in heaps with limited access of air. About a quarter of the weight of the original wood is left as charcoal.

Animal Charcoal.—By heating comparatively fresh bones in iron retorts or in iron pots.

Lampblack.—1. Very pure carbon may be obtained by transmitting the vapours of alcohol, turpentine, &c., through a red-hot porcelain tube. 2. A less pure form is obtained on heating sugar, starch, rosin, pitch, &c., in iron vessels with limited access of air. 3. A very pure carbon may be obtained by heating gas-carbon for some time to a red heat, first in a current of chlorine, and finally in air.

DRY DISTILLATION OF COAL.

Among the numerous products of this distillation, in addition to the residual coke, some are volatile at a high temperature, but condense to fluids or solids on cooling. Others are and remain gaseous. These products are usually classified under four heads:—

1. Coke.
2. Tar.
3. Ammonia water.
4. Gaseous products.

Tar.—This consists mainly of a most complicated mixture of hydrocarbons and their derivatives, among which may be mentioned, as being more especially separated and employed, benzol ($C_6 H_6$), toluol ($C_7 H_8$), naphthaline ($C_{10} H_8$), anthracine ($C_{14} H_{10}$), phenol ($C_6 H_6 O$). The separation and purification of these substances constitutes an immense industry in itself.

Ammonia Water.—This consists chiefly of carbonate, sulphide, sulphocyanide of ammonium.

Gaseous Products (Coal Gas).—These are also very numerous, but consist in the main of hydrogen (often nearly 50 per cent.), marsh gas, and carbonic oxide, with small proportions of olefiant gas ($C_2 H_4$) and its allied compounds, the vapours of benzol, and naphthaline, to the last three of which the gas chiefly owes its illuminating power. Besides these are water vapour, sulphuretted hydrogen, ammonium, carbonic anhydride, and bisulphide of carbon. These last five are regarded as impurities, and are, as far as possible, removed by various purifying processes.

The water vapour is apt to freeze in the pipes. The sulphur compounds yield sulphurous anhydride ($S O_2$) on combustion, and the ammonium compounds similarly give rise to nitrous and nitric acid. Although marsh gas, hydrogen, and carbonic oxide burn with non-luminous flame, their presence is not considered objectionable, owing to their high temperature of combustion.

All these products are subject to more or less variation in quantity, according to the coal used, and the temperature and other conditions of manufacture.

The distillation is effected in long semi-cylindrical retorts of iron or clay. The residue in the retorts consist of coke, and the volatile products are first passed through a series of tubes, in which they are cooled and the tar is deposited; next they pass through various purifying apparatus, in which the ammonia, sulphuretted hydrogen, &c., are absorbed, and the remaining gaseous products are collected in large gas-holders for distribution. In order to avoid excess of pressure in the retorts, &c., the gas is pumped out by an air-pump and forced on through the receiving portions of the apparatus, and into the gas-holder.

CARBONIC ANHYDRIDE.

(*Carbon dioxide, carbonic acid, fixed air, choke damp*) $CO_2 = 44$. *Percentage composition*, $C = 27·27$, $O = 72·72$. *Gas at ordinary temperatures; liquid at* 0° *under* 36 *atmospheres pressure; critical point*, 30·9° (p. 51). *Solid at* – 70. *Specific gravity*, 1·529 (*air* = 1), 22 ($H = 1$)*; of liquid at* – 10·8°, 0·99 (*water* = 1).

Occurrence in Nature.—Carbonic anhydride is a normal constituent of the atmosphere, of which it constitutes, on an average, 0·04 per cent. (4 in 10,000) by volume; air expired from the lungs contains from 4 to 5 per cent. It is found issuing from the earth in many places, as, for example, in the well-known *Grotto del Cane* of Naples; it is found in almost all springs, and in the form of carbonates constitutes considerable rock formations, as carbonate of calcium in limestone, marble, and chalk, and of calcium and magnesium in dolomite. The following list includes some of the more important mineral carbonates:—

Important Mineral Carbonates.

Calc-spar, arragonite, marble, limestone, chalk, &c., $CaCO_3$.

Strontianite,	$SrCO_3$	Brown spar,	$MnCO_3$
Witherite,	$BaCO_3$	Cerussite,	$PbCO_3$
Magnesite,	$MgCO_3$	Malachite,	$Cu_3(HO)_2(CO_3)_2$
Calamine,	$ZnCO_3$	White lead,	$Pb_3(HO)_2(CO_3)_2$
Siderite,	$FeCO_3$	Hydromagnesite,	$Mg_4(HO)_2(CO_3)_3$

Physical Properties.—Carbonic anhydride is a colourless gas, having a faintly acid taste and smell; at 0° under 36 atmospheres pressure, it is condensed to a colourless, oily liquid, which, if allowed to escape suddenly into the air, freezes to a white snow-like solid, producing great cold (– 79°) by its evaporation. The solid can also be obtained by cooling liquid carbonic anhydride to – 70°.

Solid carbonic anhydride, which is very volatile, may be held in the hand lightly, or even placed on the tongue with impunity, but if pressed on the skin produces a blister. It is soluble in ether, and the solution rapidly evaporates with great depression of temperature (– 100°).

Liquid carbonic anhydride has a coefficient of expansion four times as great as that of air. It is miscible in all proportions with ether, alcohol, turpentine, and bisulphide of carbon, but is insoluble in water and fatty oils. It is a bad conductor of electricity, and both in the solid and liquid form is a bad conductor of heat.

The gas is slightly soluble in water. One volume of water absorbs 1·79 volumes at 0°, and 1·002 at 15° under a pressure of 1 atmosphere. At greater pressures it dissolves the same volume; but, of course, the amount by weight which is dissolved increases as the pressure (p. 49).

Chemical Properties.—Carbonic anhydride is apparently a true anhydride, but no definite hydrate of it is known. It forms, however, a large class of compounds with basic oxides, called carbonates, corresponding to the theoretical hydrate, $H_2 C O_3$, which may be regarded as a dibasic acid, properly called carbonic acid.

An aqueous solution of litmus is reddened by the gas, but on heating the solution the gas is expelled, and the litmus resumes its original blue colour. It is rapidly absorbed by the solutions of alkaline hydrates, forming two series of salts, the acid carbonates (bicarbonates) corresponding to the formula $M H C O_3$, or neutral carbonates, $M_2 C O_3$. It is also absorbed by lime-water, or by milk of lime,* with formation of the insoluble carbonate of calcium, $Ca C O_3$, and similarly by solutions of the other hydrates of the alkaline earths. It is a weak acid, that is, it is easily expelled from its compounds by most other acids.

It is neither a combustible nor a supporter of combustion under ordinary conditions. Water containing it in solution acquires increased solvent powers.

Heated to 1300°C. it splits up into carbonic oxide and oxygen. Carbon, phosphorus, iron, &c., remove part of its oxygen forming carbonic oxide. Sodium and potassium at a red heat remove its oxygen entirely with separation of carbon.

As already stated, 1 gramme of carbon, in burning to carbonic anhydride, evolves 8,000 heat units.

Distinguishing Tests.—A colourless gas which is heavier than air and turns lime-water milky (*cf.* carbon, p. 133).

Physiological Action.—Carbonic anhydride is irrespirable, producing spasm of the glottis when concentrated, but may be breathed with impunity when much diluted with air; 3 to 4 per cent. in air acts as a narcotic poison if the air is inhaled for some time, but in such an atmosphere a candle continues to burn.† Owing to its high specific gravity, it is very liable to collect in confined, badly ventilated places

* *Milk of lime* is slaked lime mechanically mixed with water.

† An admixture of 10 per cent. and upwards proves rapidly fatal.

in which it is produced; and, hence, no such places should be entered without previous ventilation.

Preparation.—1. *By acting on almost any carbonate with almost any acid.*

2. The usual method of obtaining carbonic anhydride is to act upon marble with dilute hydrochloric acid, whereupon a brisk effervescence ensues owing to the escape of the gas. Calcium chloride and water are simultaneously formed, thus:—

$$\overset{\text{Marble.}}{Ca\,C\,O_3} + \overset{\text{Hydrochloric Acid.}}{2\,H\,Cl} = \overset{\text{Calcic Chloride.}}{Ca\,Cl_2} + \overset{\text{Water.}}{H_2\,O} + \overset{\text{Carbonic Anhydride.}}{C\,O_2}.$$

Modes of Production.—By the combustion of carbon in all its various forms, by the burning of all organic matter, by the action of nitric or sulphuric acids on charcoal, in the process of respiration, in volcanic action, by the decomposition of carbonates, by heat or acids, in the process of fermentation, in lime-kilns, as choke-damp after the explosion of fire-damp (p. 140).

CARBONIC OXIDE.

(*Carbon monoxide*) $C\,O = 28$. *Percentage composition*, $C = 42{\cdot}86$; $O = 57{\cdot}14$. *Gas at ordinary temperatures; liquid at* −190° *under* 1 *atmosphere pressure; solid at* −211°; *critical point* −139·5° (p. 51). *Specific gravity*, 0·967 (*air* = 1); 14 (*H* = 1). 11·19 *litres weigh* 14 *grammes.*

Occurrence in Nature.—Strictly speaking, carbonic oxide does not occur in nature, but it is found wherever carbonic anhydride comes into contact with glowing carbon, as in all fire-places, furnaces, &c., and especially in charcoal stoves, evincing its presence by its bright blue flame and oppressive odour.

Physical Properties.—Carbonic oxide is a colourless, tasteless gas of faint oppressive odour. It is not condensed to a liquid at a pressure of 2,790 atmospheres at ordinary temperatures, but is easily liquefied under the conditions above stated, and solidifies at a temperature of − 211°.

It is very slightly soluble in water; 1 volume of water absorbs 0·0328 volume at 0°, and 0·02311 at 20°. It is more soluble in alcohol; 1 volume of alcohol (specific gravity, 0·792) absorbs 0·204 volume from 0° to 25°. It is easily soluble in an ammoniacal solution of cuprous chloride.

Chemical Properties.—Carbonic oxide gas is inflammable, but not a supporter of combustion. It burns with a beautiful blue flame, forming carbonic anhydride; 1 gramme of carbon in burning to carbonic oxide evolves 2,433 units of heat, and the carbonic oxide thereby produced evolves, when burnt to carbonic anhydride, 5,567 units of heat.

Owing to its affinity for oxygen, it is a powerful reducing agent. It combines directly with oxygen, with explosion, under the influence of the electric spark. It also combines directly with chlorine on exposure to sunlight, forming phosgene gas ($C\,O\,Cl_2$). It unites with metallic potassium at a temperature of 80°, forming a substance whose composition is represented by the formula $C\,O\,K_2$. It is not absorbed by a solution of potassium hydroxide, but combines with the solid at a temperature of 100°, with production of potassium formate; $K\,H\,O + C\,O = H\,C\,O_2\,K$.

Distinguishing Tests.—A colourless gas of faint odour, almost insoluble in water, insoluble in solutions of the alkalies, burning with a bright blue flame, with formation of carbonic anhydride. Exploded with half its volume of oxygen, it yields its own volume of carbonic anhydride. Soluble in an ammoniacal solution of cuprous chloride. Blood shaken up with air containing even a small proportion of the carbonic oxide yields a characteristic absorption spectrum.

Physiological Action.—Carbonic oxide is a very poisonous gas, and induces giddiness, faintness, and death, when present in the air in comparatively small quantities.* In contact with the blood, it forms a compound with the hemoglobin, which shows two black absorption bands in the green portion of the spectrum, almost identical with the two bands shown by oxyhemoglobin, but not like them affected by reducing agents.

Preparation—1. *By the action of Sulphuric Acid on Oxalic Acid.*—Finely powdered oxalic acid is mixed with about six times its weight of strong sulphuric acid in a flask, which may be heated on a sand-bath. Considerable effervescence ensues, the sulphuric acid splitting up the molecule of oxalic acid (by the withdrawal of the elements of water) into water, carbonic anhydride, and carbonic oxide. If these two gases are led through a wash-bottle containing caustic potash solution, the carbonic anhydride is fixed, the carbonic oxide passing on.

$$\overset{\text{Oxalic Acid.}}{C_2H_2O_4} \quad - \quad \overset{\text{Water.}}{H_2O} \quad = \quad \overset{\substack{\text{Carbonic}\\\text{Anhydride.}}}{C\,O_2} \quad + \quad \overset{\substack{\text{Carbonic}\\\text{Oxide.}}}{C\,O.}$$

The gas may be collected over water.

2. *By the action of Sulphuric Acid on Potassium Ferrocyanide.*—One part by weight of ferrocyanide is heated with 8 to 10 parts by weight of sulphuric acid. Here, again, a complete disintegration of the

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* 0·5 per cent. rapidly fatal; particularly in presence of some CO_2; still smaller proportions after some time.

organic molecule is brought about by the sulphuric acid, with formation of carbonic oxide, and the sulphates of potassium, iron, and ammonium respectively.*

$$\overset{\text{Potassium Ferrocyanide.}}{K_4 Fe C_6 N_6, 3 H_2 O} + \overset{\text{Water.}}{3 H_2 O} + \overset{\text{Sulphuric Acid.}}{6 H_2 S O_4} =$$

$$\overset{\text{Carbonic Oxide.}}{6 C O} + \overset{\text{Potassic Sulphate.}}{2 K_2 S O_4} + \overset{\text{Ferrous Sulphate.}}{Fe S O_4} + \overset{\text{Ammonium Sulphate.}}{3 (N H_4)_2 S O_4}.$$

3. *By the action of Carbon on Carbonic Anhydride.*—If carbonic anhydride is passed over charcoal contained in a strong glass tube at a red heat, it is deprived of half its oxygen, and the carbonic oxide so formed may be collected as usual.

$$\overset{\text{Carbonic Anhydride.}}{C O_2} + \overset{\text{Carbon.}}{C} = \overset{\text{Carbonic Oxide.}}{2 C O}.$$

Other Modes of Preparation or Production.—4. *By heating to redness a mixture of Chalk and Charcoal in an iron vessel,* $CaCO_3 + C = CaO + 2 CO$. 5. *By heating a mixture of Chalk and Zinc, or Iron,* $Ca C O_3 + Fe = Ca O + Fe O + C O$. 6. *By heating a mixture of Oxide of Zinc and Charcoal,* $Zn O + C = Zn + C O$. 7. *By passing Steam over Charcoal,* $C + H_2 O = C O + H_2$. 8. *By the action of Sulphuric Acid upon a Formate,* $2 Na C H O_2 + H_2 S O_4 = 2 C O + Na_2 S O_4 + 2 H_2 O$. 9. *By the action of Sulphuric Acid upon Hydrocyanic Acid,* $H_2 O + H C N + H_2 S O_4 = C O + H_3 N . H_2 S O_4$.

MARSH GAS.

(*Methane, light carburetted hydrogen, fire-damp*) $C H_4 = 16$. *Percentage composition,* $C = 75·0$; $H = 25·0$. *Gas at ordinary temperatures. Liquid at* −164° *under* 1 *atmosphere pressure. Specific gravity of gas* 0·55 (*air*=1); 8 (*H*=1) *of liquid at* −164° 0·415 (*water*=1). 11·19 *litres weigh* 8 *grammes.*

Occurrence in Nature.—Marsh gas is found in coal-mines, and sometimes issues in large quantities from fissures in the coal ("blowers"). It is also found in some few places issuing from the earth, and rises from the mud of pools when this is stirred up—hence its name.

Physical Properties.—Marsh gas is a colourless, odourless gas, condensible to a liquid only at a temperature of −73·5° and a pressure of 56·8 atmospheres, or at −131° at a pressure of 6·7 atmospheres. It is very slightly soluble in water; 1 volume water absorbs 0·047 volume at

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* The water in this reaction is taken from that present in the sulphuric acid, even when concentrated. The reaction would be more nearly expressed as follows:—

$$K_4 Fe Cy_6, 3 H_2 O + 3 H_2 O + x H_2 S O_4 = 6 C O$$
$$+ 4 K H S O_4 + 6 N H_4 H S O_4 + Fe S O_4 + x - 11 H_2 S O_4.$$

6·2°. It is more soluble in alcohol; 1 volume absolute alcohol absorbs 0·5 volume marsh gas.

Chemical Properties.—Marsh gas is inflammable, but requires a white heat for its ignition. It burns with a yellowish, scarcely luminous flame, forming water and carbonic anhydride. It is a non-supporter of combustion. Mixed with 2 volumes of oxygen or 10 volumes of air it is dangerously explosive, but if mixed with less than 6 volumes, or more than 14 volumes, of air it will not explode. If the air, however, contains fine dust, even if this is not in itself combustible, a much more diluted mixture becomes explosive. Marsh gas forms the first member of a long series of hydrocarbons of the general formula, $C_n H_{2n+2}$, known as paraffins.

It obtains the name, fire-damp, from its occurrence in coal-mines, where it frequently gives rise to most disastrous explosions, which further give rise to a vitiated atmosphere (known as *after-damp*), containing much carbonic acid, which is irrespirable. Sir H. Davy's safety-lamp (p. 91) was designed to prevent these explosions.

Distinguishing Tests.—Inflammable; very slightly soluble in water; insoluble in solutions of alkalies or in strong sulphuric acid; exploded with oxygen, it yields water and its own volume of carbonic anhydride; mixed with 2 volumes of chlorine, it explodes when exposed to the action of sunlight or bright daylight.

Physiological Action.—Marsh gas is not poisonous, and can be breathed, when mixed with air, with comparative impunity.

Preparation.—By heating a mixture of sodium acetate, soda, and lime in a glass retort, the lime being added to modify the action of the soda on the glass. The gas may be collected over water.

Sodium Acetate.		Soda.		Marsh Gas.		Sodium Carbonate.
$Na C_2 H_3 O_2$	+	$Na H O$	=	$C H_4$	+	$Na_2 C O_3$.

2. It may be obtained chemically pure by the decomposition of zinc methyl by water.

Zinc Methyl.		Water.		Zinc Hydroxide.		Marsh Gas.
$Zn (C H_3)_2$	+	$2 H_2 O$	=	$Zn O H_2 O$	+	$2 C H_4$.

CYANOGEN.

(*κύανος, blue, and γεννάω, I produce*) *C N or Cy′*=26; *Cy*$_2$=52 *Sp. gr.* 1·8 (*air*=1); 26 (*H*=1).

Properties.—A colourless gas of peculiar odour, rather soluble in water, condensed to a liquid at a pressure of 3·6 atmospheres at 7·2°, or at ordinary pressures at a temperature of − 18°. It solidifies at − 40°. It is inflammable, burning with a peach-blossom coloured flame (purple edged with rose). Combines indirectly with hydrogen to form hydrocyanic or prussic acid (H C N). Cyanogen is a radical like *ammonium* ($N H_4$) (see p. 128); but, unlike ammonium, it plays the part of a non-metal, showing a strong analogy to the halogens (p. 199). It forms an immense series of compounds termed cyanides, which belong properly to the organic division of chemistry. It is poisonous. It owes its name to the fact that it is a constituent of Prussian blue.

Preparation—1. By heating mercuric cyanide [$Hg(CN)_2$]. This substance splits up on heating into mercury and cyanogen gas.

2. If air is passed over a mixture of potassium, carbonate, and charcoal, potassium cyanide is formed—$K_2CO_3 + 4C + N_2 = 2KCN + 3CO$.

THE ATMOSPHERE.

Physical Characters.—The atmosphere completely surrounds the globe, forming, so to speak, an aërial ocean, at the bottom of which we live, and which, if it were of uniform *density*, would have a height of about 5 miles. Air, however, being elastic, the lower layers, pressed as they are by those above, are of greater density than the upper layers, the density diminishing as we ascend. The rate of diminution is such that for every 3·4 miles of ascent, the density becomes reduced by one-half. Thus, taking the density at the sea-level as 1, it will be $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, &c., at heights of 3·4, 6·8, and 10·2, &c., miles respectively. The actual height of the atmosphere must, therefore, be considerable, and has been variously estimated at from 45 to 200 miles (calculated from duration of twilight, or heights at which shooting stars or meteorites become visible).

As we ascend, the *temperature* diminishes, though, owing to winds, in a somewhat irregular manner. Everywhere, however, a height is reached at which the temperature is at or below 0°C. all the year round. This line is at a height of about 15,000 feet in the tropics, at about 6,000 here in England, and reaches the surface of the earth at the arctic circles. Mountains reaching above that height will, as a rule, be covered with snow all the year. The actual height of the snow-line for any particular place is, however, also governed in great measure by the humidity of the air and consequent amount of rainfall or snow. Thus, on the northern, cooler slopes of the Himalayas the snow-line is several thousand feet higher than it is on the southern, warmer slope, owing to the fact that the former is exposed to the dry winds which have passed over Central Asia, while the latter is struck by the moist winds coming from the Indian Ocean and Persian Gulf.

The *weight* of a column of air of one square inch section, reaching from the sea level to the upper limit of the atmosphere, is about 15 lbs., and this is, therefore, the pressure exerted by the atmosphere per square inch of surface at the sea level. This is equal to the pressure of a column of mercury of 30 inches high (height of barometer at the sea level), or of one of water about 32 feet (extreme height to which water can be raised by a perfect suction pump).

The *total weight* of the atmosphere has been calculated at 5,000,000,000,000,000 tons, or about 27,000,000 tons per square mile of surface.

The *specific gravity* of air, or rather of air perfectly dry and free from carbonic anhydride and other admixtures, used to be, and is still often taken as the unit with which to compare the specific gravity of gases and vapours. One litre of such air at 0°C. and 760 mm. pressure weighs, in the latitude of Paris, 1·2932 grammes. 100 cubic inches weigh, at the same temperature and pressure, 32·586 grains.

The *colour* of the air in large masses is blue (explained as due to the presence of ozone or of excessively minute particles, cause of the blue colour of the sky). Aqueous vapour absorbs chiefly the blue constituents of sunlight (cause of orange sunsets).

The *expansion or contraction* of air is equal to 0·003655 of its volume at 0°C. for every 1°C. rise or fall respectively. It follows Boyle's law up to very considerable pressures, but departs from it at very high pressures. It has been liquefied, and even solidified by aid of the extremely low temperature produced by the evaporation of liquid hydrogen.

Water, shaken up with an unlimited quantity of air, dissolves relatively more oxygen than nitrogen; the proportion existing between these two gases in the dissolved air being as 32·5 to 67·5,[*] as against the proportion of 21 to 79 in atmospheric air. As oxygen passes more readily through a caoutchouc membrane than nitrogen, the proportion of oxygen to nitrogen can be increased to a considerable degree by making the air pass through a series of such membranes.

Chemical Characters.—The composition of atmospheric air is of extreme simplicity, as far as its main constituents are concerned, but of extraordinary complexity, if its more minute, though not necessarily less important, components are taken into account.

Average Composition of the Atmosphere by volume.

Oxygen,	20·61
Nitrogen,	77·95
Carbonic anhydride,	0·04
Aqueous vapour,	1·40
Nitric acid,	traces.
Ammonia,	traces.
	100·00

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[*] This is exactly in proportion to the solubility of the two gases taken by themselves.

Atmospheric air, then, consists mainly of a mixture of nitrogen, oxygen, aqueous vapour, carbonic anhydride, and ammonia. Besides these five, which we may term the normal constituents, being never absent, there are often found, according to seasons, circumstances, or locality, ozone, nitrates and nitrites, hydrocarbons, sulphates, chloride of sodium—the latter particularly near the sea, particles of carbon, meteoric and other mineral dust, pollen of flowers, spores and germs of a great variety of low organisms, innoxious and noxious, and, in towns, particles of almost every solid material in use in the town. In the neighbourhood of certain centres of industry we may find sulphurous acid, chlorine, hydrochloric acid, arsenious acid, &c., &c.

Oxygen and Nitrogen.—The relative amount of these two gases varies, under ordinary conditions, in the open air, within very narrow limits only, at whatever part of the earth the air may be collected. This proportion is nearly as 21 to 79 by volume. In confined places the proportion of oxygen frequently sinks below this, but even a slight diminution soon affects our senses. The two gases, notwithstanding the near constancy in their proportion, are not chemically united, but are only mechanically mixed, as is proved by the following facts: 1st, When air is shaken up with water, each gas is dissolved in exact accordance with its special coefficient of solubility; 2nd, each gas retains its special rate of diffusion; 3rd, the two gases are not present in any atomic proportion; 4th, oxygen and nitrogen, when mixed in the proportion in which they are contained in atmospheric air, suffer no alteration, either in temperature or in volume, and the mixture possesses all the characters of atmospheric air.

The following figures will serve to give some idea of the proportion of oxygen found at various times and places; they are taken from the works of Bunsen, Regnault, Frankland, and Angus Smith:—Marburg (1846), 20·9965; Paris, 20·913 to 20·999; Geneva, 20·909 to 20·993; London (St. Bartholomew's Hospital), 20·885 to 20·999; London (18,000 feet high), 20·885; Manchester, 20·820 to 20·980; Scotch Moors, 20·999; Atlantic Ocean, 20·918 to 20·985; Antarctic Seas, 20·86 to 20·94; summit of Pinchincha (16,000 feet), 20·948 to 20·988; pit of a theatre, 11.30 p.m., 20·740; small room with petroleum lamp (6 hours), 20·830; Court of Queen's Bench, Feb. 2, 1866, 20·650; in sumps or pits in a mine, 20·140; when candles cease to burn, 18·500; worst specimen of air in mine examined by Angus Smith, 18·270.

Oxygen and nitrogen may be estimated by various means, carbonic acid having previously been absorbed—

1st, By absorbing the oxygen by means of an alkaline solution of pyrogallic acid; 2nd, by passing dried air over red-hot copper, weighing the nitrogen which passes on (by collecting it in a previously exhausted and weighted glass balloon, which also serves as aspirator), and determining the increase in weight suffered by the copper; 3rd, and most accurately, by mixing a known volume of air with hydrogen, exploding the mixture, and measuring the diminution in volume produced—one-third of this is oxygen.

In methods 1 and 3 the oxygen is estimated directly by measure, and the remainder is taken as nitrogen; in method 2 both the oxygen and nitrogen are weighed.

Aqueous Vapour.—This varies greatly, but amounts on an average to about 1½ per cent. by volume. If too little moisture is present an unpleasant parching sensation is experienced, while if too much is present it produces an uncomfortable feeling of closeness in warm weather, and a chilly feeling in cool weather. The most comfortable feeling is experienced when the air contains rather more than half the amount of moisture it would be capable of holding, or, as it is generally expressed, when the degree of humidity amounts to about 60 per cent. The actual amount of moisture which air is capable of containing is governed solely by the temperature—*i.e.*, the tension of aqueous vapour at the temperature of the air (p. 37). Air, which at any given temperature contains as much moisture as it is capable of holding, is said to be *saturated* with moisture, and the proportion of this possible maximum, which it may hold at any time, or its *humidity*, is expressed as a percentage of this maximum. Thus air, the humidity of which is 60 per cent., contains three-fifths of all the moisture it could possibly hold at the particular temperature at which it is; humidity, therefore, expresses a relative, and not an absolute quantity.

The actual amount of moisture contained in air at any given time may be estimated:—

1st. By passing a given volume of air through tubes containing chloride of calcium or sulphuric acid, and weighing the increase in weight produced in these tubes. 2nd. By gradually lowering the temperature of a bright metallic surface until a film of moisture begins to be deposited on it (dew point); the temperature at which the metal then is marks the point at which the air experimented on would be saturated, and the amount present may be found from any table giving the tension of aqueous vapour at that temperature (Regnault's hygrometer), and by various other means.

Carbonic Anhydride.—The proportion of carbonic anhydride varies in the open country between 3 to 4 volumes per 10,000 volumes of air; over the sea it is slightly higher during the day, and slightly lower during the night. In towns the proportion is generally higher, more particularly during foggy weather, and in inhabited rooms it is higher still, and in crowded places may rise as high as 30 to 50 volumes per 10,000. Air becomes unpleasant, and even unwholesome, when it contains more than 10 volumes of carbonic anhydride per 10,000 volumes, if it is produced by the breathing of men or animals, not because this small amount of carbon dioxide is in itself injurious, but because under these circumstances there are always present other emanations which, although their actual amount cannot at present be estimated with any degree of exactness, have an injurious effect. Carbonic acid affords thus a useful indirect measure of the amount of such substances present which cannot be directly estimated. In order to keep the air in inhabited places pure the amount of fresh air admitted per hour should not be less than 2,000 cubic feet per person present in the room.

Carbonic anhydride may be estimated by various means—

1st. By passing a known volume of air through caustic potash, and estimating the increase in weight produced. 2nd. By shaking up a known volume of air with a known amount of lime or baryta water, and measuring the decrease in alkalinity produced by means of a very dilute standard acid. 3rd. Roughly (*a*), by producing a certain standard degree of turbidity in a given volume of baryta water, and measuring the amount of air necessary for this; (*b*) by measuring the maximum quantity of air, which, when shaken up with a given volume of baryta water, will not produce any appreciable turbidity. Thus, if when ½ ounce of baryta water (containing about ½ per cent. of baryta) be shaken up with air in a bottle of 7 ounces capacity, no turbidity is produced if the air does not contain more than 3 volumes of carbonic acid per 10,000 volumes; if no turbidity is produced with a bottle of only 4·5 ounces capacity, the air does not contain more than 5 volumes per 10,000, &c. This furnishes a very useful test for regulating the ventilation in hospital wards, &c. As long as no turbidity is produced by the shaking up of ½ ounce baryta water in a bottle of 2·5 ounces capacity, the air contains not more than 10 volumes of carbonic acid in 10,000 volumes, and ventilation may be assumed to be good; if, however, a turbidity is produced, and more than 10 volumes of carbonic acid are present, ventilation is defective.

Ammonia.—Ammonia is present in the air, probably in the form of carbonate, nitrate, or nitrite, in the proportion of about 5 volumes to 10,000,000 volumes of air. Nevertheless, minute as the quantity appears in comparison with the other constituents, the vegetation on the globe is, in great measure, dependent on it for its supply of nitrogen.

Ammonia may be estimated by passing a known volume of air through pure dilute hydrochloric acid, and estimating the amount of ammonia absorbed by the acid by means of what is known as the Nessler test.*

Ozone.—This is always found in the pure air of the open country or over the sea, rarely or never in the air of towns, owing to its powerful chemical affinities and the organic matters always found in town air. The absolute amount has not been fairly determined, but it probably rarely exceeds one part per 1,000,000. Qualitatively, its presence can be demonstrated by the various ozone papers (Ozone, p. 96). Its presence in air is due to electric discharges; hence, it is always found in greater quantity directly after thunderstorms. Its presence is also due to the oxidation of essential oils and other odoriferous compounds given out by plants and flowers. Although present

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* *Nessler Test.*—A strongly alkaline solution of mercuric iodide in iodide of potassium which strikes a brown colour when added to very dilute solutions of ammonia or its salts, the depth of which depends on the amount of ammonia present.

only in very minute quantity it has an important function as a purifying agent of the atmosphere.

Solid Floating Particles — (*a*) *Chloride of Sodium.* — Sodium, no doubt in the form of chloride, is almost always present in the air, even many miles distant from the sea; occasionally, as after heavy storms, in notable quantities at great distances inland, due to the sea spray carried off by the wind. Its presence is easily seen by examining the flame of a Bunsen burner, which, in England, will always show the yellow sodium flame.

(*b*) *Other Solids.*—A bright beam of light passed through air almost always reveals the presence of innumerable floating particles (motes in the sunbeam), by means of which the path of the beam can be traced; air perfectly free from floating particles does not show the track of the beam (Tyndall). They may further be demonstrated by various means—

1st. A large volume of air is passed, by means of an aspirator, through a tube loosely plugged with collodion cotton; the particles are arrested by the cotton, and if, after a sufficient volume of air has passed, this is dissolved in a mixture of two volumes of ether to one volume of alcohol, they remain behind, and can be collected by subsidence and examined under the microscope. 2nd. A little glycerine is spread over the centre of a microscope slide, which is then either simply put into the place, the air of which is to be examined (glycerine upwards), or a slight current of air is directed against it by a glass funnel. After a time a cover glass is put over the glycerine, and the particles adhering to it examined with the microscope. 3rd. A small quantity of water is put into a clean bottle and shaken up, the stopper of the bottle is removed, the air in the bottle renewed either by blowing or sucking the air out by means of a bellows, the water again shaken up, and the process repeated until the water has become sufficiently turbid to furnish a deposit, which can be examined by the microscope.

Any one of these three methods will readily show the enormous variety of solid particles constantly floating in the air, and will enable the careful microscopist to recognise many definite forms.

These particles, minute as they are, nevertheless represent some of the most powerful and far-reaching agencies of nature. Without their presence organic matters would not putrefy, vinous and other fermentations would not take place, wounds would heal without sloughing or production of pus; while, by their means, many infectious disorders are generated and spread. It is to the recognition of the wonderful effects of these ever-present, though minute, agents that we owe some of the most important advances of modern surgery (the so-called antiseptic treatment of Professor Lister, for example), and of preventive medicine.

Estimation of Organic Matters in Air.—Many attempts have been made to estimate the amount of organic matters present in atmospheric air under various conditions, but as yet without complete success; three methods, however, may be briefly described—

1st. Dr. Angus Smith proposed to estimate the relative amount of organic matters in air by the reducing effect they exert on permanganate of potassium. For this object a perfectly clean bottle is filled—best by means of a kind of bellows arranged for sucking out the air of the bottle—with the air to be examined, a small but known measure of a solution of permanganate, acidulated with sulphuric acid, is introduced, and the bottle shaken for some minutes. If the red colour of the permanganate has not been destroyed, the air in the bottle is renewed by means of the bellows, and the bottle once more shaken; this renewing of the air and shaking is repeated until the red colour of the permanganate is discharged, the number of times the bottle has to be refilled to effect this being noted. The purer the air the greater, the more impure, speaking generally, the smaller, the number of times required to effect this.

2nd. According to a method devised by the authors, air is passed by suction first through a tube filled with previously ignited asbestos, to arrest the floating particles, the current is next divided into two by means of a T piece. One of these currents is passed directly through a Pettenkofer tube containing baryta water; the other has to pass, firstly, through a heated tube containing pure oxide of copper, and then through a second Pettenkofer tube also containing baryta water, the two currents being measured by carefully regulated meters. The carbonic acid absorbed in the two tubes is then estimated by special analytical methods; the difference between the two amounts gives the carbonic acid produced by the organic matter contained in the air. If desired, the organic matter arrested by the asbestos tube may be burnt in a current of oxygen, and the carbonic acid produced estimated. The proportion of organic matter found by the authors in London air corresponds to about 5 volumes of CO_2 for every 100,000 volumes of air.

3rd. A method for approximately estimating the amount of nitrogenised organic matter contained in air is based on Wanklyn's process for water analysis. A large volume of air is shaken up with pure water, and the water is then distilled; at first by itself, or with the addition of carbonate of soda only, a strong solution of alkaline permanganate is then added, and the distillation continued. This second distillate is collected separately, and the ammonia it contains estimated by Nessler's test. The purer the air the less ammonia will be found in this distillate.

BORON.

(*Arabian word búráq, white; whence Latin, borax*) *B*=11. *Solid at ordinary temperatures. Triad.*

Occurrence in Nature.—Boron is not found free, but only in combination with oxygen, as boric acid (*q.v.*), or as borate of sodium (borax), magnesium, or calcium.

Physical Properties.—Boron occurs in the form of a brown amorphous powder. It is very difficultly fusible. The so-called crystallised form, prepared by dissolving boron in molten aluminium, has been shown to be a compound of boron and aluminium, and not pure boron. Boron is insoluble in water. The specific heat of boron, which, at ordinary temperatures, is only 0·25, is doubled at higher temperatures.

Chemical Properties.—Boron burns in air, forming boric anhydride, It is converted by nitric acid into boric acid. It burns also in chlorine, forming boron trichloride. It is especially characterised by its power of combining with nitrogen at a high temperature, forming boron nitride ($B N$).

Preparation—1. *Amorphous Boron.*—By fusing a mixture of boric acid and sodium. If to ten parts of boric acid six parts of sodium are added, and the mixture thrown into a red-hot iron crucible and covered with a layer of common salt, boron is set free, and may be obtained in the amorphous form by treatment of the fused mass with hydrochloric acid.

BORIC OXIDE.

(*Boric anhydride*) $B_2 O_3 = 70$.

Properties.—Colourless, transparent, glass-like, deliquescent substance, becoming converted into boracic acid in contact with water.

Preparation.—By heating boric acid to a red heat.

BORIC ACID.

(*Boracic acid, hydrogen borate*) $B O_3 H_3 = 62$. $[B (O H)_3]$. *Percentage composition*, $H = 4{\cdot}84$; $B = 17{\cdot}74$; $O = 77{\cdot}42$. *Solid at ordinary temperatures.*

Occurrence in Nature.—The occurrence of this substance is very remarkable; it is found in solution in certain hot lagoons in Tuscany and some other volcanic districts into which it is carried by jets of steam (called suffioni or fumaroli) issuing from fissures in the soil. It is also found as sodium borate (*Tincal*, $Na_2 O, 2 B_2 O_3, 10 H_2 O$) in Thibet, and in combination with sodium and calcium as *boronatrocalcite* $[2 (Na Ca 3 B O_2) 3 B_2 O_3, 18 H_2 O]$ in Peru.

Physical Properties.—Boric acid crystallises in white tabular forms, difficultly soluble in cold water but more easily soluble in hot. It is also soluble in alcohol, which solution, if ignited, burns with a peculiar green flame. The aqueous solution cannot be evaporated without loss, owing to its characteristic property of volatilising with the escaping steam, as strikingly illustrated by its natural occurrence.

Chemical Properties.—Boric acid is a weak acid, but, owing to its stability at a high temperature, is capable of ejecting most acids from combination at a red heat. It forms a large series of salts derived from three hydrates, namely, ordinary tribasic boric acid, $B(OH_3)$; metaboric acid, $BO.OH$; and pyroboric acid, $H_2B_4O_7$. Its sodium salt, $Na_2B_4O_7$, is a common reagent in the laboratory. This compound, when fused, forms a clear glass which, at a red heat, dissolves many metallic oxides with characteristic colours (borax beads).

Distinguishing Tests.—A white, crystalline substance, which swells up on heating. Difficultly soluble in water. Soluble in alcohol, to the flame of which it imparts a green colour. Its solution in water, especially when acidified with hydrochloric acid, imparts to turmeric paper a reddish tint, appearing more clearly on drying.

Physiological Action.—It has marked antiseptic properties.

Preparation.—By addition of hydrochloric acid to a hot concentrated solution of sodium borate. On cooling, the boric acid crystallises out and may be purified by recrystallisation.

Manufacture.—1. In Tuscany the boric acid is obtained by condensing the steam-jets (soffioni) in water; the solution of boric acid thus obtained being afterwards concentrated to crystallisation by the heat of the same steam-jets. 2. It is also manufactured from borax and borate of lime by treatment with an acid.

NITRIDE OF BORON—$BN = 25$.

Properties.—Boron nitride is a white, amorphous powder, insoluble in water or dilute acids or alkalies. Heated with water to 200° in closed tubes, it is decomposed with formation of boric acid and ammonia.

Preparation.—1. By heating amorphous boron in a current of air or nitrogen. 2. By heating borax with twice its weight of chloride of ammonium in a platinum crucible, and extracting the fused mass with dilute hydrochloric acid.

SILICON.

(*Silex, flint*) $Si = 28$. *Solid at ordinary temperatures. Specific gravity of graphitic form*, 2·49 (*water*=1). *Specific heat*, 0·203 *at* 232°; 0·138 *at* 1000°. *Tetrad.*

Occurrence in Nature.—Next to oxygen, silicon is the most abundantly occurring and widely diffused element known. The element does not occur free, but always in combination with oxygen as silica (SiO_2), which substance, either alone or combined with various metals, forms an immense series of well-known and widely distributed minerals, some few of which are enumerated below. Silica is also found in the vegetable kingdom, especially in the grasses and allied plants, and exists in the feathers of some birds.

Natural Forms of Silica ($Si\ O_2$).

Quartz or Rock Crystal.
Amethyst.
Agate.
Chalcedony.
Onyx.
Cornelian.
Opal.
Jasper.
Flint.
Sand.
Sandstone.
Infusorial Earth.

Of these, quartz and amethyst occur in well-shaped crystals belonging to the hexagonal system (six-sided prisms). Agate and chalcedony are a mixture of crystallised and amorphous silica.

The following compounds of silica are broadly classed as aluminic and magnesic silicates, but mostly contain, in addition to these elements, sodium, potassium, calcium, iron, manganese, &c. Their formulæ are very varied and very complicated, and by no means thoroughly known.

Some Common Silicates.

Aluminic Silicates.

Beryl.
Clay.
Felspar.
Garnet.
Jade.
Lapis lazuli.
Mica.
Pumice-stone.
Slate.
Topaz.

Magnesic Silicates.

Asbestos.
Augite.
Hornblende.
Meerschaum.
Olivine.
Steatite (French Chalk, Soap-stone, &c.)
Talc.

Physical Properties.—Silicon, like carbon, an element which it much resembles in its properties, is known in three remarkable modifications. As *amorphous silicon*, it presents the appearance of a dark-brown powder. As *graphitic silicon*, it forms scaly crystals, resembling graphite, which scratch glass and are infusible. As *diamond silicon*, it resembles crystallised hematite in appearance, scratches glass, and fuses at a temperature approaching that of cast iron. The specific gravity of graphitic silicon is 2·49 (water = 1). All three forms are insoluble in water. The amorphous form is soluble in a solution of hydrochloric acid, with evolution of hydrogen. The specific heat of silicon, like that of boron and carbon, follows Dulong and Petit's law only at higher temperatures.

Chemical Properties.—Amorphous silicon, when heated in air, burns and is superficially converted into silica. Heated in chlorine, it burns and forms tetrachloride of silicon ($Si\,Cl_4$). If strongly heated out of contact with air, it becomes much denser and is no longer combustible. It is unacted upon by nitric or sulphuric acid, but is converted by hydrochloric acid at a high temperature into a chloride.

Preparation—1. *Amorphous Silicon.*—By heating the double fluoride of potassium and silicon (potassium fluosilicate, $2\,K\,F,\ Si\,F_4$) in a strong glass tube with its own weight of potassium, the silicon is set free, and the reaction is accompanied with much heat. If the mass is treated with water the amorphous silicon remains behind undissolved.

Potassium Fluosilicate.		Potassium.		Silicon.		Potassium Fluoride.
$2\,K\,F,\ Si\,F_4$	+	$2\,K_2$	=	Si_2	+	$6\,K\,F$.

2. *Diamond Silicon.*—By introducing into a red-hot crucible three parts of potassium fluosilicate, one part of sodium in small pieces, and one part of granulated zinc, and heating to fusion; on slowly cooling a button of zinc is formed, interspersed with needle-shaped crystals, which may be freed from the zinc by treatment with hydrochloric acid. 3. *Graphitic Silicon.*—By fusing in a Hessian crucible five parts of potassium silicate ($K_2\,Si\,O_3$) with ten parts of cryolite ($3\,Na\,F,\ Al\,F_3$) and one part of aluminium, on treatment of the fused mass with hydrochloric acid scaly crystals of graphitic silicon remain.

SILICA.

$Si\,O_2 = 60$. *Percentage composition,* $Si = 46{\cdot}66$; $O = 53{\cdot}34$.

Occurrence in Nature (see Silicon, p. 149).

Physical Properties.—Natural silica, as already stated (p. 150), is found either amorphous or in well-formed crystals. Artificially prepared it is always amorphous, and either combined with water, when it presents the appearance of a jelly, or anhydrous, when it is a white powder of specific gravity, 2·66, and fusible at only very high temperatures. Its many modifications, with the exception of that form which is precipitated from a solution of an alkaline silicate by hydrochloric acid, are insoluble in water and all acids but hydrofluoric.

The amorphous varieties are soluble in boiling solutions of the alkalies, the crystalline varieties are insoluble in such.

Chemical Properties.—Silica is an acid-forming oxide, and combines with water to form numerous hydrates, and in combination with various bases gives rise to an extensive and very complicated series of salts, many of which constitute some of the more commonly occurring substances of the mineral kingdom. The composition of these hydrates and of the silicates, as these salts are called, is very imperfectly known; many silicates are known which correspond to the hydrate SiO_2, H_2O or $[SiO(OH)_2]$, many also which may be referred to a hydrate $SiO_2, 2H_2O$ or $[Si(OH)_4]$, and, again, others which apparently belong to various intermediate forms. A solution of silica in water (see Preparation 3) has a feebly acid reaction; it is very apt to gelatinise.

Distinguishing Tests.—A gelatinous substance or white powder, which, after evaporation with hydrochloric acid to complete dryness on a water-bath, is insoluble in all acids but hydrofluoric.

Preparation—1. *Of hydrated silica by decomposition of silicon tetrafluoride with water.*—If a mixture of powdered glass, fluor-spar (CaF_2), and strong sulphuric acid be heated in a flask, the delivery tube of which dips into a cylinder containing water, the gaseous tetrafluoride of silicon which is formed is decomposed by the water with formation of gelatinous silica and hydrofluosilicic acid. The reaction may be expressed as follows:—

a. By the action of the sulphuric acid on fluor-spar hydrofluoric acid is formed, which reacts on the silica of the glass with formation of silicon tetrafluoride, thus—

$$\overset{\substack{\text{Hydrofluoric}\\\text{Acid.}}}{4HF} + \overset{\text{Silica.}}{SiO_2} = \overset{\text{Water.}}{2H_2O} + \overset{\substack{\text{Silicon}\\\text{Tetrafluoride.}}}{SiF_4}.$$

b. The silicon tetrafluoride coming into contact with water is decomposed as follows:—

$$\overset{\substack{\text{Silicon}\\\text{Tetrafluoride.}}}{3SiF_4} + \overset{\text{Water.}}{4H_2O} = \overset{\substack{\text{Hydrated}\\\text{Silica.}}}{H_4SiO_4} + \overset{\substack{\text{Hydrofluosilicic}\\\text{Acid.}}}{2H_2SiF_6}.$$

It is necessary to make the end of the delivery tube dip first into mercury, over which water is standing, or else the mouth of the tube becomes stopped.

2. *Of anhydrous silica by precipitating a soluble silicate with hydrochloric acid and evaporating to dryness.*—If pure mineral silica, such as rock crystal, is fused with sodium carbonate, soluble sodium silicate (Na_2SiO_3) is formed, and from a strong solution of this salt silica may be precipitated by hydrochloric acid, and if the whole be evaporated to dryness, and the dry residue extracted with hydrochloric acid, pure insoluble silica remains behind.

3. *Of a solution of silica in water by diffusion.*—If a dilute solution of an alkaline silicate be added to an excess of hydrochloric acid, the silica is retained in solution, and if this solution is subjected to dialysis (p. 48), by placing it in a dialyser with a parchment paper bottom, and floating in water, the chloride and excess of hydrochloric acid diffuse through, leaving a solution of pure silica in the dialyser.

SILICON HYDRIDE.

(*Siliciuretted hydrogen*) $SiH_4 = 32$. *Percentage composition*, $H = 12{\cdot}5$; $Si = 87{\cdot}5$. *Gas at ordinary temperatures.*

Physical Properties.—A colourless gas, insoluble in water.

Chemical Properties.—This gas, if impure, is (like phosphoretted hydrogen), spontaneously inflammable in contact with air. If passed through a red-hot glass tube it is decomposed into its constituent elements with deposition of amorphous silicon.

Preparation.—By the action of diluted hydrochloric acid and magnesium silicide (obtained by heating together magnesium chloride, sodium silico-fluoride, common salt, and sodium).

Magnesium Silicide.		Hydrochloric Acid.		Magnesium Chloride.		Silicon Hydride.
Mg_2Si	+	$4HCl$	=	$2MgCl_2$	+	SiH_4.

SULPHUR.

[*Sal, salt, and* πῦρ, *fire, brimstone* (*brennstein, burning stone*)] $S = 32$; $S_2 = 64$. *Solid at ordinary temperatures; melting point of octohedral*, 114·5°; *of prismatic*, 120°; *boiling point*, 440°. *Specific gravity of solid octohedral*, 2·045; *of prismatic*, 1·98; *of plastic*, 1·957 (*water* = 1); *of vapour at* 850°, 2·2 (*air* = 1); 32 ($H = 1$). *Dyad to hexad. Specific heat of octahedral*, 0·1776; *of prismatic*, 0·1844.

Occurrence in Nature.—Sulphur occurs in considerable quantities and widely distributed in combination, but somewhat locally, though also in large quantity as an element. In this latter form it is found in fine crystals, sometimes quite pure, sometimes intimately mixed with gang, chiefly in Sicily and Iceland, but also in some other parts of Europe and in the craters of extinct volcanoes in the Pacific Islands. In direct combination with certain metals it occurs in the following well-known mineral sulphides known as *pyrites* or *blendes*, iron pyrites (FeS_2), copper pyrites ($CuFeS_2$), galena or lead sulphide

(Pb S), zinc blende (Zn S); as sulphates in gypsum ($CaSO_4, 2H_2O$), heavy spar ($BaSO_4$), &c., &c., in immense quantities. In the animal kingdom it is found as a constituent of complex carbon compounds, in albumen, hair, and bile; and in the vegetable kingdom it enters into the composition of certain essential oils, as those of mustard, garlic, &c.

Physical Properties.—Sulphur is pre-eminently distinguished by the variety of its allotropic modifications, each involving, and, in fact, dependent upon, physical differences. To obtain, therefore, a complete insight into its various physical properties, as a whole, it will be necessary to describe each modification separately.

The following general statement regarding it may, however, be made:—It is dimorphous. Its colour varies from white (when very finely divided) to pale lemon and amber yellow. It is devoid of taste and smell. In some forms it is transparent, in others opaque to light. In all forms, with one exception (plastic sulphur), it is brittle. It is insoluble in water and, according to condition, slightly soluble in alcohol and ether, more so in turpentine, benzole, and (but sometimes insoluble) in bisulphide of carbon. It is a bad conductor of heat and electricity. It becomes negatively electric when rubbed.

The specific gravity of its vapour at temperatures a little above its boiling point is about 96 ($H=1$), a density corresponding to six atoms in the molecule; but at the temperature of 850° to 1000° its specific gravity=32, and this corresponds to two atoms only (p. 62).

Behaviour to Heat.—If any one of the more common forms of sulphur be heated, it first melts at 114°·5 into a pale yellow, thin fluid of appreciably less specific gravity than that of the solid sulphur. On further heating, the colour becomes gradually darker, and the liquid assumes a more and more viscid consistency, until, at a temperature of 200°, it has the colour of dark treacle, and is so thick that the vessel containing it can be inverted without the sulphur flowing out; on still further increasing the temperature, the sulphur becomes more fluid again, but never so fluid as at the melting point. At 440° it boils, becoming converted into a dark brown, heavy vapour, and may, in fact, be distilled. On allowing the sulphur to cool gradually, it passes through these changes in the reverse order. The temperature at first falls rapidly, becomes stationary at 200°, again sinks rapidly, and the fluid finally solidifies to prismatic sulphur.

1. *Natural or Octahedral Modification.*—This, as the first name implies, is the variety of sulphur found native, and all the other varieties have, at ordinary temperatures, a greater or less tendency to revert to this form. It crystallises in the rhombic system, generally in octahedra,

with end planes, has a specific gravity of 2·045, melts at 114·5°C., and boils at 440°C. When dissolved in bisulphide of carbon, or other solvents, it crystallises from these in the same form.

2. *Prismatic Modification.*—Sulphur, when allowed to crystallise from the melted condition, assumes the form of prisms belonging to the oblique prismatic (monoclinic) system. In this form it has a specific gravity of 1·98, and melts (according to Brodie) at 120°, but boils like the first variety at 440°. At ordinary temperature the prisms, which at first are transparent, become opaque, and are then found to have changed, without alteration of outward shape, into a conglomeration of octahedra, the prismatic having changed into the octahedral variety. On the other hand, octahedral sulphur, when kept for some time at a temperature of 100°C., gradually changes into the prismatic variety.

3. *Plastic Modification.*—If, however, the sulphur is cooled rapidly from a temperature of about 400°, by pouring it in a thin stream into cold water, it does not become hard and brittle, but assumes the form of a soft, elastic solid, known by the name of plastic sulphur. In this condition it has a specific gravity of 1·957, and is insoluble in bisulphide of carbon. At ordinary temperatures this variety changes slowly, at a somewhat higher temperature rapidly, into the octahedral sulphur. This change, however, is never complete; but, when, after the plastic sulphur has become hard, the mass is treated with bisulphide of carbon, the greater portion (the octahedral part) dissolves, leaving always more or less of an insoluble powder, known as *amorphous sulphur.*

4. *Amorphous Modification.*—If the brittle mass obtained by exposing plastic sulphur to the air for several days is treated with bisulphide of carbon, a portion of it is found to be insoluble. It is a buff-coloured amorphous powder.

5. *Milk of Sulphur.*—Milk of sulphur is also an amorphous variety, but soluble in bisulphide of carbon. It is this variety which is chiefly employed for internal use. It is a white impalpable powder, made by precipitating a solution of a soluble polysulphide with an acid. The sulphide nearly always employed is the pentasulphide of calcium, and if the acid used for the precipitation is hydrochloric acid, the precipitate obtained is nearly pure sulphur; if, on the other hand, sulphuric acid is employed, the milk of sulphur is obtained mixed with a large proportion of crystalline sulphate of calcium up to 50 per cent., and even more.

6. *Flowers of Sulphur.*—This variety of sulphur is produced by rapidly cooling the vapour of sulphur. It is obtained on a large scale during the distillation of sulphur, while the chamber into which the vapour

is passed is at a low temperature. It is in the form of globules, consisting chiefly of crystalline sulphur, but containing always more or less of insoluble amorphous sulphur.

7. *Ordinary Roll Sulphur.*—This, when first cast, is of the prismatic form, changing in time to the octahedral.

8. *Other Varieties.*—With regard to other varieties, we need only mention that *red* (?) and *black* and *blue* modifications are said to exist.

All these modifications may be classified according to Berthelot under two groups:—

a. Electro-negative forms. Soluble in carbon bisulphide.	1. *Octahedral* or native sulphur. 2. *Prismatic* sulphur. 5. *Milk of Sulphur* (amorphous).
b. Electro-positive forms. Insoluble in carbon bisulphide.	3. *Plastic* sulphur. 4. *Amorphous* sulphur. *a.* From plastic sulphur. *b.* From chloride of sulphur.

Electro-negative sulphur includes all varieties of sulphur separated from combination with electro-positive elements and such as are, like these, soluble in carbon bisulphide. Electro-positive sulphur includes all forms separated from combination with electro-negative elements and such as are, like these, insoluble in carbon bisulphide.

Chemical Properties.—Sulphur resembles oxygen in many of its chemical properties, forming, with other elements, compounds (sulphides) analogous to both basic and acid oxides. It is both a combustible and a supporter of combustion. Its vapour takes fire in air a little above the melting point of the solid, and burns with a pale blue flame, sulphurous anhydride ($S\,O_2$) resulting from its combination—a gas recognised by its peculiar odour.

In pure oxygen sulphur burns with still greater brilliancy (see oxygen), the same gas resulting. Sulphur also combines directly with chlorine, hydrogen, phosphorus, with carbon under absorption of heat, and with many metals—*e.g.*, copper, silver, iron, sodium, &c., which burn brilliantly in its vapour with evolution of much heat, sulphides resulting.

Distinguishing Tests.—Sulphur may be distinguished from all other substances as a solid of somewhat varied form (see physical properties), which, when heated, melts, ignites, and burns with a blue flame, disappearing entirely, and forming sulphurous anhydride recognised by its well-known powerful and suffocating smell.

Physiological Action.—Internally in small doses it acts as a gentle stimulant to the secreting organs, in larger doses, 3 to 4 drachms, as a mild purgative. Externally, it forms a valuable application in various skin diseases, and is applied to plants as a protection or cure of various fungoid diseases.

Preparation.—By crystallisation, sublimation, distillation or precipitation.

Manufacture.—Sulphur is obtained from native sulphur by simple melting or distillation, or is manufactured from iron pyrites by distillation. Melted and cast into wooden moulds, it is known as *roll sulphur;* or condensed in cool chambers in the form of coarse powder, it is known as *flowers of sulphur;* precipitated from polysulphides (see physical properties), it constitutes *milk of sulphur*, (see also p. 214).

SULPHUROUS ANHYDRIDE.

(*Sulphur dioxide*) $S O_2 = 64$. *Percentage composition*, $S = 50$, $O = 50$. *Gas at ordinary temperatures. Liquid under* 3 *atmospheres pressure, or at* $- 10°$; *solid at* $- 75°$. *Specific gravity*, 2·247 ($air = 1$); 32 ($H = 1$); *of liquid*, 1·49 ($water = 1$). 11·19 *litres weigh* 32 *grammes*.

Occurrence in Nature.—Sulphurous anhydride is found in volcanic gases.

Physical Properties.—Sulphurous anhydride is a colourless gas of pungent odour (familiar in the smell of burning sulphur) and of unpleasant taste, and belongs to the easily condensible gases, requiring only a pressure of 3 atmospheres at ordinary temperatures to condense it to a limpid and very volatile liquid, which produces a cold of $-60°$ by its evaporation, and becomes solid at $- 75°$. It is very soluble in water, which at 8° takes up 58·6 times its volume, at 15°, 43·5 volumes.

Chemical Properties.—Sulphurous anhydride forms no definite or stable hydrate, but its salts correspond to the formula of the hydrate $H_2 S O_3$. If a saturated solution of sulphurous anhydride is exposed to a temperature of 0°, a crystalline hydrate is formed, the composition of which is, however, not definitely known.

It is a non-inflammable gas, and eminently a non-supporter of combustion in the ordinary sense. It is, in fact, used as a fire-extinguisher.

A piece of litmus paper plunged into the moist gas is first reddened and then bleached. This bleaching action is very characteristic of sulphurous anhydride; like chlorine, it bleaches vegetable colouring-matters; but, unlike chlorine, which acts chiefly by oxidation, it bleaches by forming colourless and, more or less, soluble compounds.

with the colouring-matter (the colour being restored by addition of a strong acid or alkali). It is used largely in the bleaching of straw and woollen goods. Owing to its great attraction for oxygen it is a powerful reducing agent.

Physiological Action—*On plants.*—It is a most powerful poison to plants, even when very much diluted with atmospheric air (1 volume in 40,000). *On man.*—In the concentrated form it excites spasm of the glottis when inhaled, and when diluted acts as a local irritant. It is a most powerful antiseptic and deodorant, and the most convenient gaseous disinfectant. For the purpose of disinfecting rooms, 1 lb. of sulphur should be burnt for every 1000 cubic feet of space.

Preparation.—1. For laboratory use. From sulphuric acid by the action of copper. If sulphuric acid be heated in a flask with copper, it is deprived of part of its oxygen with formation of cupric sulphate, water, and sulphurous anhydride, according to the equation—

Copper.		Sulphuric Acid.		Cupric Sulphate.		Water.		Sulphurous Anhydride.
Cu	$+$	$2\,H_2SO_4$	$=$	$CuSO_4$	$+$	$2\,H_2O$	$+$	SO_2.

The gas may be first washed by passage through water, and then passed into distilled water if a solution is required or collected over mercury, after passage over chloride of calcium, if required dry.

Other Modes of Preparation.—2. From sulphuric acid by the action of mercury. 3. From sulphuric acid by the action of charcoal, $C + 2\,H_2SO_4 = 2\,SO_2 + CO_2 + 2\,H_2O$. 4. On the large scale by burning sulphur in air or oxygen, $S + O_2 = SO_2$. 5. By roasting iron or copper pyrites, $4\,FeS_2 + 11\,O_2 = 2\,Fe_2O_3 + 8\,SO_2$.

SULPHURIC ANHYDRIDE.

(*Sulphur trioxide*) $SO_3 = 80$. *Percentage composition*, $S = 40$, $O = 60$. *Crystalline solid; melting point*, 16°; *boiling point*, 46°.

Physical Properties.—Sulphuric anhydride crystallises in prisms, which melt at 16°, the oily fluid so formed boiling at 46°. If heated to 25° it is transformed into an isomeric modification which melts at 50°, and then resumes the ordinary form.

It is soluble in water, with evolution of much heat and formation of the hydrate SO_3, H_2O.

Chemical Properties.—Sulphuric anhydride is a true acid-forming oxide possessing great attraction for water, and combining with it, as already stated, with great evolution of heat becoming converted into sulphuric acid. It hisses when plunged into water. If a drop of water be let fall on some of the anhydride, explosion may occur, accompanied with a flash of light.

If passed through a red-hot tube in the form of vapour, it is decomposed into sulphurous anhydride ($S O_2$) and oxygen.

Preparation.—1. By cautious distillation of Nordhausen sulphuric acid. 2. By passing sulphurous anhydride and oxygen over heated platinum sponge or platinized asbestos. 3. By distilling sulphuric acid with phosphoric anhydride.

SULPHURIC ACID.

(*Hydric sulphate, oil of vitriol*) $H_2 S O_4 = 98$. $[S O_3 . H_2 O; S O_2 (O H)_2]$. *Percentage composition*, $H = 2{\cdot}1$; $S = 32{\cdot}6$; $O = 65{\cdot}3$, *or* $S O_3 = 81{\cdot}63$; $H_2 O = 18{\cdot}37$. *Liquid at ordinary temperatures; boiling point*, 338°. *Specific gravity at* 0°, 1·854 (*water* = 1); *of vapour*, 24·5 ($H = 1$).

Occurrence in Nature.—Sulphuric acid occurs free in some springs of volcanic origin, in very minute quantity. In combination with the alkali metals, it is widely diffused in the animal and vegetable kingdoms, and with the metals of the alkaline earths forms some common rocks, such as gypsum, $Ca S O_4 2 H_2 O$, and anhydrite, $Ca S O_4$, heavy spar, $Ba S O_4$, and celestine, $Sr S O_4$.

Physical Properties.—Sulphuric acid, when pure, is a colourless, dense, oily fluid, nearly twice as heavy as water; specific gravity 1·85. It freezes at 0° and boils at 338°, becoming more or less dissociated into sulphuric anhydride and water vapour. At a somewhat lower temperature, already it gives off dense white fumes of a highly pungent and irritating odour.

It is miscible with water in all proportions, with evolution of great heat, forming with it various hydrates (see below).

Chemical Properties.—Sulphuric acid is essentially a dibasic acid and forms a large series of acid and neutral salts, called *sulphates*, by the replacement of one or two of its hydrogen atoms respectively, but also gives rise to salts corresponding to an acid of higher basicity (see below).

A very characteristic property of sulphuric acid is its great attraction for water. Thus, it is highly hygroscopic, attracting moisture from the air, and is used, for this purpose and for the abstraction of water of crystallisation or for the drying of solids, in *dessicators*, or for the drying of gases.

Its action on organic matter is highly destructive, generally causing it to *char*, that is to carbonise, and, especially with respect to those substances containing hydrogen and oxygen, which elements it abstracts from them in the proportion in which they form water, *e.g.*—

$$\begin{array}{ccccc} \text{Cane Sugar.} & & \text{Water.} & & \text{Carbon.} \\ C_{12}H_{22}O_{11} & - & 11\,H_2O & = & C_{12}. \end{array}$$

$$\begin{array}{ccccccc} \text{Oxalic Acid.} & & \text{Water.} & & \text{Carbonic Oxide.} & & \text{Carbonic Anhydride.} \\ C_2H_2O_4 & - & H_2O & = & CO & + & CO_2. \end{array}$$

As already stated, it mixes with water in all proportions with evolution of great heat,[*] and considerable contraction of volume; thus, 50 cubic centimetres of sulphuric acid added to 50 cubic centimetres of water yield only 97·1 cubic centimetres of the mixture after cooling. It forms several hydrates; among these is one corresponding to the formula, $H_2SO_4 . H_2O$, which, on cooling, yields crystals melting at 7·5°. The hydrate, $H_2SO_4 . 2\,H_2O$ may be produced by heating dilute sulphuric acid in vacuo to 100°, until it ceases to lose weight. It has a specific gravity of 1·632, and boils at 175·5. This hydrate forms salts referable to a hexabasic acid, H_6SO_6, or $S(HO)_6$, and corresponds also to the maximum contraction of a mixture of sulphuric acid and water, amounting in this case to 8 per cent.

It is the strongest known acid, expelling all other acids from their compounds when in aqueous solution.

The action of the metals upon it differs according to the metal and the concentration of the acid. Thus, copper, mercury, and silver cause the concentrated acid to yield sulphurous anhydride with formation of the corresponding sulphates and water. Zinc causes it to yield a mixture of hydrogen and sulphuretted hydrogen, but zinc and dilute acid form hydrogen and zinc sulphate (see preparation of hydrogen, p. 100). Carbon, in the form of charcoal, acts upon the concentrated acid with the formation of sulphurous anhydride, carbonic anhydride, and carbonic oxide. Phosphorus separates sulphur from it and combines with its oxygen.

Distinguishing Tests.—The strong acid is an oily, strongly-acid liquid, which evolves much heat when mixed with water, chars wood and paper, &c. The dilute acid acts similarly on concentration and yields,

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[*] In mixing sulphuric acid with water, the acid should always be added to the water in a thin stream with constant stirring. Otherwise, there is danger of spirting, or the heat evolved may crack the vessel in which the mixture is made.

with soluble barium salts, a white precipitate, insoluble in acids and which, fused on charcoal with sodium carbonate, is *reduced* to a sulphide. The same precipitate is yielded by all soluble sulphates.

Physiological Action.—Concentrated, it is an intense corrosive poison, but much diluted, it is used medicinally as a refrigerant and astringent.

Manufacture.—The manufacture of sulphuric acid may be briefly expressed as *the oxidation of sulphurous anhydride by means of nitric acid in the presence of water vapour, and excess of atmospheric air.* These substances are simultaneously introduced into leaden chambers of great dimensions, often from 12 to 15 feet high, 15 to 20 feet broad, and from 150 to 300 feet long. The sulphurous anhydride is formed by burning sulphur or, more commonly, by roasting pyrites; the nitric acid by the action of sulphuric acid upon saltpetre, the water being introduced in the form of steam or spray. The reactions which ensue, with the ultimate formation of sulphuric acid, are undoubtedly of a very complicated character, but their simplest aspect may be represented by the following equations:—

1. Oxidation of sulphurous anhydride by nitric acid to sulphuric acid, with formation of nitric peroxide.

Sulphurous Anhydride.		Nitric Acid.		Sulphuric Acid		Nitric Peroxide.
SO_2	+	$2HNO_3$	=	H_2SO_4	+	$2NO_2$.

2. Oxidation of sulphurous anhydride by nitric peroxide in presence of steam, and formation of nitric oxide.

Sulphurous Anhydride.		Nitric Peroxide.		Water.		Sulphuric Acid.		Nitric Oxide.
SO_2	+	NO_2	+	H_2O	=	H_2SO_4	+	NO.

3. Oxidation of nitric oxide to nitric peroxide by atmospheric oxygen.

Nitric Oxide.		Oxygen.		Nitric Peroxide.
NO	+	O	=	NO_2.

4. Repetition of 2.

Nitric oxide thus acts as a carrier of oxygen and, theoretically, is capable of converting an unlimited proportion of sulphurous acid into sulphuric acid in the presence of air and steam, but practically the amount so convertible is limited.

This is owing chiefly to the necessity of having a constant current of air passing through the chambers, which carries off some of the nitric peroxide. In order to reduce this loss as much as possible the following ingenious devices are resorted to:—The gases escaping from the chambers are passed through a tower (Gay-Lussac's tower) filled with coke or pebbles, down which concentrated sulphuric acid is constantly allowed to run, and this absorbs the nitric peroxide. The sulphuric acid, after it has been saturated with nitric peroxide in the Gay-Lussac's tower, is mixed with chamber acid, and caused to flow down a similar tower (Glover's tower), through which the hot gases produced by the roasting of the iron pyrites are forced to pass before entering the leaden chambers. In this tower (Glover's) the nitric peroxide absorbed in the Gay-Lussac tower is reduced by the sulphurous anhydride to nitric oxide, which is again carried into the chamber, while the sulphuric acid (equation 2) is at the same time concentrated by the hot gases in contact with it.

The manufacture is often accompanied by formation of white crystals, which, according to more recent researches, have the composition, $N_2 O_3, 2 S O_3$, or $[2 S O_2, 2 N O_2, O]$, and this substance forms crystalline compounds with varying proportions of sulphuric acid; hence its composition has been very variously stated. In contact with water, it is decomposed into sulphuric acid, nitric acid, and nitric peroxide.

Whatever may be the nature of the reactions involved, their ultimate result is the formation of sulphuric acid, of specific gravity about 1·5, at the bottom of the chambers (chamber acid). This is drawn off and concentrated by evaporation in leaden pans to a specific gravity of 1·71 (brown acid), and finally in platinum stills until of specific gravity 1·84. This is the sulphuric acid of commerce and contains 98 per cent. of acid ($H_2 S O_4$), but also a number of impurities, such as lead, arsenic, nitric acid, &c.

Preparation.—1. By the distillation of commercial acid and rejection of the first portion of the distillate. 2. The manufacture of sulphuric acid may be experimentally illustrated by passing into a large glass flask, fitted with five openings, sulphurous anhydride, water vapour, nitric oxide, and air, leaving one opening as a vent. If the sulphurous anhydride and nitric oxide are first passed into the apparatus with comparatively little moisture, white crystals are formed and coat the sides of the flask, but are broken up in contact with steam, and dilute sulphuric acid collects at the bottom of the flask.

NORDHAUSEN SULPHURIC ACID.

(*Disulphuric, pyrosulphuric, fuming sulphuric acid*) $H_2 S_2 O_7 = 178$.
$[H_2 S O_4 . S O_3]$.

This acid may be regarded as a compound of sulphuric acid with sulphuric anhydride, or, as derived from two molecules of sulphuric acid, by the abstraction of one molecule of water. It is a brown fuming liquid of specific gravity 1·9, freezes at 0° in colourless crystals, and is split up easily by heat into sulphuric anhydride and sulphuric acid.

Preparation.—It was formerly prepared at Nordhausen, in Saxony, by the distillation of ferrous sulphate:—the salt ($Fe S O_4 . 7 H_2 O$)

is first dried, and then has the composition $Fe\,S\,O_4\,.\,H_2\,O$. This on heating yields, in the first place, sulphurous anhydride and water, leaving in the retort hexabasic ferric sulphate—

$$\overset{\text{Ferrous Sulphate.}}{2\,Fe\,S\,O_4\,.\,H_2\,O} \quad = \quad \overset{\text{Hexabasic Ferric Sulphate.}}{Fe_2\,S\,O_6} \quad + \quad \overset{\text{Sulphurous Anhydride.}}{S\,O_2} \quad + \quad \overset{\text{Water.}}{H_2\,O.}$$

The hexabasic sulphate on further heating breaks up into sulphuric anhydride and ferric oxide—

$$\overset{\text{Hexabasic Ferric Sulphate.}}{Fe_2\,S\,O_6} \quad = \quad \overset{\text{Ferric Oxide.}}{Fe_2\,O_3} \quad + \quad \overset{\text{Sulphuric Anhydride.}}{S\,O_3.}$$

But the acid is now made by mixing sulphuric anhydride and sulphuric acid in the proper proportions.

A salt corresponding to this acid may be obtained by careful heating of the acid sodium sulphate—

$$\overset{\text{Acid Sodium Sulphate.}}{2\,Na\,H\,S\,O_4} \quad - \quad \overset{\text{Water.}}{H_2\,O} \quad = \quad \overset{\text{Sodic Pyrosulphate.}}{Na_2\,S_2\,O_7.}$$

which salt, when more strongly heated, breaks up into sodium sulphate and sulphuric anhydride.

$$\overset{\text{Sodic Pyrosulphate.}}{Na_2\,S_2\,O_7} \quad = \quad \overset{\text{Sodic Sulphate.}}{Na_2\,S\,O_4} \quad + \quad \overset{\text{Sulphuric Anhydride.}}{S\,O_3.}$$

THIOSULPHURIC* ACID.

(*Hyposulphurous acid*) $H_2\,S_2\,O_3 = 114$. $[SO_2\,.\,S\,H\,.\,O\,H]$.

This acid is only known in combination. If hydrochloric acid be added to a solution of one of its salts, sulphur is precipitated, and sulphurous anhydride is liberated. The alkaline thiosulphates (hyposulphites) find an extensive use in photography, owing to the property they possess of dissolving silver salts, and as an antichlore, *i.e.*, for counteracting the injurious action of residual chlorine in goods bleached by the use of bleaching powder.

Preparation.—1. By digesting sodium sulphite with sulphur. If potassium or sodium sulphite in solution is digested with sulphur, the sulphur is dissolved, and the thiosulphate formed can be obtained by crystallisation.

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* *θειον, sulphur.*

$$\overset{\substack{\text{Sodium}\\\text{Sulphite.}}}{Na_2SO_3} + \overset{\text{Sulphur.}}{S} = \overset{\substack{\text{Sodium}\\\text{Thiosulphate.}}}{Na_2S_2O_3}.$$

2. By passing sulphurous anhydride into a solution of sodium sulphide. The reaction takes place as follows:—

$$\overset{\substack{\text{Sodium}\\\text{Sulphide.}}}{2Na_2S} + \overset{\substack{\text{Sulphurous}\\\text{Anhydride.}}}{3SO_2} = \overset{\substack{\text{Sodium}\\\text{Thiosulphate.}}}{2Na_2S_2O_3} + \overset{\text{Sulphur.}}{S}.$$

3. By oxidising solutions of metallic sulphides in water, *e.g.*:—

$$2Na_2S + 2O + H_2O = Na_2S_2O_3 + 2NaHO.$$

Other compounds of Sulphur with Oxygen and Hydrogen.—Besides the above acid, a great many more exist, of which we may mention the following:—

Hydrosulphurous acid (properly called Hyposulphurous),	H_2SO_2.
Dithionic acid,[*]	$H_2S_2O_6$.
Trithionic acid,	$H_2S_3O_6$.
Tetrathionic acid,	$H_2S_4O_6$.
Pentathionic acid,	$H_2S_5O_6$.

SULPHURETTED HYDROGEN.

(*Hydrogen sulphide*, *Sulphydric acid*, *Hydrosulphuric acid*) $H_2S = 34$. *Percentage composition*, $H = 5{\cdot}88$; $S = 94{\cdot}12$. *Gas at ordinary temperatures; liquid under* 15 *atmospheres pressure; solid at* − 85°. *Specific gravity*, 1·177 (*air* = 1), 17 (H = 1).

Occurrence in Nature.—Hydrogen sulphide occurs in certain waters (Harrogate, &c.), probably owing to the reduction of sulphates by decaying organic matter and subsequent decomposition of the sulphide by carbonic anhydride; it is a constituent of volcanic gases.

Physical Properties.—Hydrogen sulphide is at ordinary temperatures a colourless gas of a most offensive odour (somewhat familiar as the odour of rotten eggs). At a pressure of from 15 to 16 atmospheres it is condensed to a colourless, mobile liquid of specific gravity, 0 9; at − 85° it freezes to a crystalline solid, which becomes gaseous with explosive violence if the pressure be removed.

Water takes up 2 to 3 times its volume, according to temperature, and this solution is much used as a reagent in the laboratory. It is more soluble in alcohol.

Chemical Properties.—Hydrogen sulphide is a combustible gas burning with a blue flame, with formation of sulphurous anhydride (SO_2) and water, but depositing sulphur when burnt with an incom-

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[*] *θεῖον, sulphur.*

plete supply of air. Its solution, in contact with air, becomes milky on standing, by deposition of sulphur, especially if the bottle containing it is not filled entirely, but contains air ($H_2S + O = S + H_2O$). Under certain conditions it may be oxidised to sulphuric acid. Its ignition-temperature is comparatively low, since it will take fire when brought into contact with a glowing coal.

It belongs to the class of *acids* (moistened litmus being reddened by it), and forms a large and important series of salts called sulphides. It is a comparatively weak acid, its salts being decomposed by carbonic anhydride.

In some of its chemical characters it resembles water. Thus, with the alkali metals, it yields sulphydrates and sulphides analogous to the hydrates and oxides, thus:—

$$K + H_2S = KHS + H.$$
$$K_2 + H_2S = K_2S + H_2.$$

It is decomposed by heat. Chlorine, bromine, and iodine decompose it, forming sulphur and hydrochloric, hydrobomic, and hydriodic acids respectively (*q.v.*). Potassium burns with great energy in the gas, becoming converted into potassic sulphide, and leaving an equal volume of hydrogen. Mixed with sulphurous anhydride, and the mixture ignited, water is formed and sulphur deposited; in presence of moisture the same change is produced gradually; hence the offensive smell of hydrogen sulphide may be quickly removed in a room by burning sulphur or by scattering a solution of sulphurous acid. With fuming nitric acid it explodes with separation of sulphur and formation of nitrous anhydride.

Distinguishing Tests.—A colourless gas of very characteristic odour which blackens paper moistened with lead acetate solution.

Physiological Action.—Hydrogen sulphide is an irrespirable and very poisonous gas—a small percentage in air already producing serious effects. It acts upon the colouring matter of the blood.

Preparation and Formation — 1. *By acting on ferrous sulphide with sulphuric acid or hydrochloric acid.* The ferrous sulphide is introduced in small quantities into any one of the forms of apparatus used for generating hydrogen, and may be either treated with sulphuric acid diluted with three times its bulk of water, or the lumps may be just covered with water and strong sulphuric acid added in small quantity. A copious evolution of gas is obtained, double decomposition ensuing according to the equation.

$$\underset{\text{Sulphide.}}{\overset{\text{Ferrous}}{FeS}} + \underset{\text{Acid.}}{\overset{\text{Sulphuric}}{H_2SO_4}} = \underset{\text{Sulphate.}}{\overset{\text{Ferrous}}{FeSO_4}} + \underset{\text{Sulphide.}}{\overset{\text{Hydrogen}}{H_2S.}}$$

The gas may be collected over warm water, or, if a solution is required, may be passed through a series of bottles containing distilled water.

2. *By acting on antimony sulphide with hydrochloric acid.* Hydrogen sulphide obtained as above is apt to contain impurities (among others, hydrogen), so that if the gas is required absolutely pure, it is best to take antimony sulphide and heat it in a flask with hydrochloric acid sufficiently diluted to prevent its fuming.

The reaction may be expressed as follows :—

Antimony Sulphide.		Hydrochloric Acid.		Antimony Chloride.		Hydrogen Sulphide.
Sb_2S_3	$+$	$6HCl$	$=$	$2SbCl_3$	$+$	$3H_2S$.

3. Sulphuretted hydrogen is formed when sulphur vapour and hydrogen are led over porous substances (*e.g.*, pumice), or when nascent hydrogen and sulphur come into contact. 4. When hydrogen is passed over some sulphides. 5. By the action of zinc on concentrated sulphuric acid.

HYDROGEN PERSULPHIDE.

[?] $H_2S_2 = 66$. *Fluid at ordinary temperatures. Specific gravity,* 1·769 (*water* = 1).

Properties.—A yellow oily fluid of intensely irritating odour. It is inflammable. It decomposes spontaneously, or on warming, into sulphuretted hydrogen and sulphur. It is an extremely active chemical substance, and bears a most remarkable resemblance in its properties to its analogue, peroxide of hydrogen (H_2O_2). Its composition is, however, by no means well known, and later researches seem to indicate the formula, H_2S_3.

Preparation.—By slowly pouring a solution of a polysulphide of calcium into an excess of dilute hydrochloric acid, whereupon milk of sulphur (p. 155) is precipitated, and an impure hydrogen persulphide is formed and collects at the bottom of the vessel.

CARBON BISULPHIDE.

(*Carbon disulphide, Sulpho-carbonic anhydride*) $CS_2 = 76$. *Percentage composition,* $C = 15·79$; $S = 84·21$. *Liquid at ordinary temperatures; boiling point,* 46°. *Specific gravity of liquid,* 1·271 (*water* = 1); *of vapour,* 2·63 (*air* = 1); 38 ($H = 1$).

Physical Properties.—Bisulphide of carbon is a colourless, mobile liquid. It usually possesses a most repulsive odour, but this is said to be due to impurities in the form of organic compounds of sulphur, and if the liquid be shaken with mercury the unpleasantness is largely removed. Its freezing point is very low, and is not known with certainty. It is very volatile, boiling at 46°, and produces great cold by its evaporation.

It is a highly refractive liquid, its *index of refraction* being 1·68. It is insoluble in water, through which it sinks when mixed with it, but is soluble in alcohol and ether in all proportions. It possesses special solvent powers, readily dissolving sulphur, phosphorus, iodine, and many organic compounds, such as oils and resins.

Chemical Properties.—Bisulphide of carbon is a very inflammable substance, the ignition point of its vapour being as low as 150°, and burns with a pale blue flame, forming carbon dioxide ($C\,O_2$) and sulphur dioxide ($S\,O_2$). Its vapour, when mixed with air, is highly explosive, and the mixture is especially dangerous, owing to the low ignition point of the vapour.

It is an analogue of carbonic anhydride, and forms sulpho-salts, called sulpho-carbonates, on account of their analogy to carbonates, *e.g.*, calcium sulpho-carbonate, $Ca\,C\,S_3$. It is generally reckoned to belong to the organic division of chemistry.

Physiological Action.—Anæsthetic in small quantity, but poisonous in larger quantity, when inhaled. It is sometimes employed for killing insects. It possesses antiseptic properties.

Preparation.—By passing the vapour of sulphur over charcoal at a red heat.

SELENIUM.

(σελήνη, *the moon*) $Se = 79$, $Se_2 = 158$. *Solid at ordinary temperatures; melting point a little above* 100°; *boiling point about* 700°. *Specific gravity*, 4·3. *Dyad to hexad. Sp. heat*, 0·0762.

Selenium occurs in small quantity in certain pyrites. When these pyrites are used in the manufacture of sulphuric acid, the selenium is burnt with the sulphur, but is reduced in the lead chambers, and is found among the sludge collecting at the bottom of the chambers. This sludge forms the material for its preparation.

Selenium closely resembles sulphur, forming similar compounds with oxygen and hydrogen, &c., which are, in all respects, analogous to the corresponding sulphur compounds; but are readily distinguished from these last by the ease with which their selenium can be obtained by the action of reducing agents and of certain metals, such as zinc. It is a very bad conductor of electricity. This is especially the case with crystalline selenium, which is remarkable for its varying conductivity under variation in the intensity of light to which it is exposed—the conductivity increasing with the intensity of the light. (Photophone.)

TELLURIUM.

(*Tellus, the earth*) $Te = 128$, $Te_2 = 256$. *Solid at ordinary temperatures. Specific gravity*, 6·2 (*water* = 1); *melting point about* 500°. *Dyad to hexad. Specific heat*, 0·0474.

This element is found, in very small quantity, native and in combination with certain metals, such as silver, gold, lead, and bismuth. It closely resembles selenium, and forms analogous compounds.

CHLORINE.

(χλωρὸς, *green*) $Cl = 35{\cdot}5$, $Cl_2 = 71$. *Gas at ordinary temperatures. Liquid at* − 40°, *or at mean temperature under pressure of* 4 *atmospheres; solid at* − 102°. *Specific gravity*, 2·41 (*air* = 1); 35·5 ($H = 1$); *of liquid*, 1·38 (*water* = 1). *Monad.* 11·19 *litres weigh* 35·5 *grammes.*

Occurrence in Nature.—Chlorine does not occur free in nature, but is found in large quantity, and widely distributed, in combination chiefly with sodium, as sea salt or common salt in sea-water and in almost all spring or river waters; as rock salt in enormous deposits in various parts of the world. In combination with magnesium and calcium it is associated with the above, and is found in small quantities combined with various other metals. Combined with hydrogen in hydrochloric acid it occurs in the gases of volcanoes. As hydrochloric acid it is also a constituent of gastric juice.

Physical Properties.—Chlorine is a yellowish green gas of pungent and irritating odour and peculiar taste, which may be easily liquefied to a yellow liquid somewhat heavier than water under the conditions above stated.

To obtain liquid chlorine, chlorine hydrate, which has been pressed between blotting-paper, is enclosed in a Faraday tube (p. 127) which is hermetically sealed. The hydrate, on heating to 35°, gives up its chlorine, which is liquefied by its own pressure; or dry charcoal may be saturated with chlorine gas in a Faraday tube, and will yield liquid chlorine under the same conditions.

Chlorine is rather soluble in water (sufficiently to make its collection over *warm* water necessary); at 10°, 1 volume of water absorbs 2·58 volumes chlorine, and at 15°, 2·36 volumes.

Chemical Properties.—Chlorine is characterised by great powers of combination. Its attraction for hydrogen is particularly strong. Thus, mixed with hydrogen, it combines with it, with explosion, under the influence of sunlight, the electric light, magnesium light, &c., or, in presence of platinum sponge, or by the application of a spark or flame, or more or less gradually in diffused light, forming hydrochloric acid gas. It is even capable of abstracting hydrogen from many compounds containing it, with formation of hydrochloric acid. It decomposes water with liberation of oxygen.* The ordinary solution of chlorine in water, known as *chlorine water*, decomposes gradually in the presence of

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* Many oxidisable substances may be oxidised indirectly by the action of chlorine in the presence of water; thus, if chlorine is passed into a solution of sulphurous anhydride, it converts it into sulphuric acid—

$$SO_2 + Cl_2 + 2\,H_2O = H_2SO_4 + 2\,HCl.$$

diffused sunlight—the chlorine combining with the hydrogen of the water and oxygen being set free. Owing to this fact, chlorine acts indirectly as an oxidising agent in the presence of water, and its remarkable bleaching action on vegetable colouring matters is often due to their destruction by the oxygen so evolved, but sometimes also to a replacing of their hydrogen by chlorine. If paper moistened with turpentine ($C_{10} H_{16}$) be dipped into the gas, it combines with the hydrogen of the turpentine with much heat and flame, and carbon is separated.* For a similar reason a taper burns in it with a smoky flame. Its action on ammonia has been already referred to (see Nitrogen, p. 114).

Chlorine is not inflammable, *i.e.*, it is not a combustible in the ordinary sense of the term. It will burn, however, in an atmosphere of hydrogen. Its attraction is not confined to hydrogen. It unites directly with sulphur. Phosphorus, sodium, copper, zinc, bismuth, arsenic, antimony, &c., take fire in the gas-forming chlorides. With water, at a temperature below 0°, it forms a hydrate, having the composition $Cl_2, 10\, H_2 O$. It is rapidly absorbed by lime (see Bleaching Powder, p. 174). Direct compounds of chlorine are called chlorides.

Distinguishing Tests.—Chlorine may be distinguished from all other substances as a heavy yellow-green gas of pungent odour, somewhat soluble in water, which explodes when mixed with an equal volume of hydrogen on being exposed to direct sunlight or strong artificial light, and which in the presence of water bleaches vegetable colouring matters. It first reddens, then bleaches litmus paper in the presence of moisture; it liberates iodine from iodide of potassium; its aqueous solution dissolves gold.

Physiological Action.—Chlorine acts very violently upon the lungs, producing even in small quantity violent cough and choking, with tightness of the chest, and often inducing for some days many of the symptoms of catarrh (known as a *chlorine cold*).

Owing to its action on organic matter, both as an oxidising agent, or by the abstraction of hydrogen, chlorine is a valuable disinfectant or destroyer of disease germs, for which purpose it may be most readily prepared by method 4 (see below).

Preparation—1. *From Hydrochloric Acid by the action of Dioxide of Manganese.*—The dioxide is introduced into a flask, and strong hydro-

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* When 1 volume of chlorine is mixed with 1 volume of ethylene ($C_2 H_4$), the two gases rapidly unite with formation of an oily liquid, ethylene dichloride ($C_2 H_4 Cl_2$); but if 2 volumes of chlorine are mixed with 1 volume of ethylene, and the mixture is set fire to, the chlorine and hydrogen combine, and all the carbon is separated ($C_2 H_4 + 2\, Cl_2 = 4\, H Cl + C_2$).

chloric acid poured upon it. Through the cork passes a delivery tube and thistle funnel, by means of which more hydrochloric acid can be added if required. By heating the flask on a sand-bath chlorine gas is copiously evolved, and after passage through a wash-bottle containing a little water, it may be collected either over hot water or, more conveniently, by downward displacement of air. If required dry it may be passed through a tube or tubes containing calcium chloride or pumice-stone moistened with sulphuric acid. It cannot be collected over mercury since it combines with this metal at ordinary temperatures.

In the reaction which occurs it is probable that tetrachloride of manganese is first formed, but, at the temperature of the action, splits up into dichloride of manganese and chlorine, according to the equations—

$$\overset{\substack{\text{Dioxide}\\ \text{of Manganese.}}}{MnO_2} + \overset{\substack{\text{Hydrochloric}\\ \text{Acid.}}}{4HCl} = \overset{\substack{\text{Manganese}\\ \text{Tetrachloride.}}}{MnCl_4} + \overset{\text{Water.}}{2H_2O}$$

$$\overset{\substack{\text{Manganese}\\ \text{Tetrachloride.}}}{MnCl_4} = \overset{\substack{\text{Manganese}\\ \text{Dichloride.}}}{MnCl_2} + \overset{\text{Chlorine.}}{Cl_2}.$$

2. *From Common Salt by the action of Dioxide of Manganese and Sulphuric Acid.*—One part by weight of dioxide of manganese is mixed with four parts of finely powdered common salt, the mixture is introduced into a flask, and two parts of strong sulphuric acid are added. The flask is heated on a sand-bath, and the gas collected as in the previous experiment.

$$\overset{\substack{\text{Manganese}\\ \text{Dioxide.}}}{MnO_2} + \overset{\substack{\text{Sodium}\\ \text{Chloride.}}}{2NaCl} + \overset{\substack{\text{Sulphuric}\\ \text{Acid.}}}{3H_2SO_4} = \overset{\substack{\text{Hydric Sodic}\\ \text{Sulphate.}}}{2NaHSO_4} + \overset{\substack{\text{Manganese}\\ \text{Sulphate.}}}{MnSO_4}$$

$$+ \overset{\text{Water.}}{2H_2O} + \overset{\text{Chlorine.}}{Cl_2}.$$

3. *By heating Platinic Chloride*—

$$\overset{\substack{\text{Platinum}\\ \text{Tetrachloride.}}}{PtCl_4} = \overset{\substack{\text{Platinum}\\ \text{Dichloride.}}}{PtCl_2} + \overset{\text{Chlorine.}}{Cl_2}.$$

4. *By acting on Bleaching Powder or its solution with excess of dilute nitric or sulphuric acid* (see p. 174).

Manufacture.—1. Generally by preparation 1; the resulting chloride of manganese is treated with lime in slight excess, and air is blown through the mixture. In the presence of the calcium hydroxide the precipitated monoxide of manganese is converted into manganese dioxide, which may be used over again (Weldon's process).

2. By passing a current of hydrochloric acid and air through

chambers filled with brick-work, at from 373° to 400°, impregnated with a solution of subchloride of copper; the latter serves as a carrier of oxygen from the air to the hydrogen of the hydrochloric acid, liberating the chlorine (Deacon's process).

(*a.*) $2\ Cu_2\ Cl_2 + 4\ H\ Cl + O_2 = 4\ Cu\ Cl_2 + 2\ H_2\ O.$

(*b.*) $2\ Cu\ Cl_2 = 2\ Cu_2\ Cl_2 + Cl_2.$

HYDROCHLORIC ACID.

(Muriatic[*] acid, Spiritus salis fumans) $H\ Cl = 36{\cdot}5$. *Percentage composition*, $H = 2{\cdot}75$, $Cl = 97{\cdot}25$. *Gas at ordinary temperatures. Liquid at* 10° *under* 40 *atmospheres pressure, or at* – 102°; *solidifies at* – 115·7°; *melts at* – 112·5°. *Specific gravity*, 1·25 (*air* = 1), 18·25 (H = 1). 11·19 *litres weigh* 18·25 *grammes.*

Occurrence in Nature.—Hydrochloric acid is found in the animal body as a constituent of gastric juice. It occurs in the gases of volcanoes.

Physical Properties.—Hydrochloric acid is a colourless gas of very hygroscopic nature, forming a cloud in contact with moist air, and possesses a penetrating and pungent odour. At 10° and a pressure of 40 atmospheres, or by exposure to a cold of – 102° at ordinary pressures, it is condensed to a colourless, highly refrangible liquid.

Like ammonia, it is characterised by its extreme solubility in water, but the specific gravity of the solution increases with increase of saturation (*cf.* ammonia, p. 127); 1 volume of water at 10° absorbs 418 volumes of the gas, forming 1·34 volumes of solution of specific gravity, 1·21, and containing about 42 per cent. of its weight of the gas. At 0°, 1 volume water absorbs 500 volumes. It is also very soluble in alcohol; 1 volume alcohol (specific gravity, 0·836) absorbs 327 volumes of the gas.

A concentrated aqueous solution when heated first parts with some of the dissolved gas, and when of specific gravity about 1·19 begins to boil at 62°, the boiling point rising to 110°, at which temperature a solution of specific gravity, 1·10, and corresponding approximately to the hydrate, $H\ Cl,\ 8\ H_2\ O$, distils over unchanged. The solution of the gas in water is colourless, very acid, fumes in contact with air, and has a pungent and irritating odour.

Chemical Properties.—Hydrochloric acid gas is neither inflammable nor a supporter of combustion. The moist gas and the solution redden litmus strongly, and exhibit all the characteristics of an acid.

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[*] Muria, *brine.*

The *aqueous solution* dissolves many metals, such as the metals of the alkalies and alkaline earths, magnesium, zinc, aluminium, tin, and iron, easily, at ordinary temperatures, with evolution of hydrogen and formation of the corresponding chlorides. On heating it dissolves lead and, in contact with air, also copper. With most metallic oxides it forms the corresponding chlorides and water. With some peroxides (*e.g.*, $Ba\,O_2$) it forms peroxide of hydrogen and a chloride, and with others (*e.g.*, $Mn\,O_2$) it forms a chloride, free chlorine, and water (*cf.* p. 95). It acts on many sulphides at ordinary or slightly elevated temperatures, with formation of hydrogen sulphide and the corresponding chloride. It has a decomposing action on many organic substances.

The gas behaves with zinc and iron, &c., like the aqueous solution, but liquefied hydrochloric acid is unacted upon by these metals.

If moist chlorine is transmitted through a red-hot porcelain tube, hydrochloric acid is formed and oxygen liberated. If hydrochloric acid and air are passed through such a tube, chlorine is liberated and water formed. The composition of hydrochloric acid gas may be analytically determined by agitating the dry gas with sodium amalgam, when sodium chloride is formed and the gas is reduced to half its volume, the residual gas being hydrogen. Zinc and iron, as above stated, yield hydrogen and a chloride in contact with the gas or aqueous solution. The presence of both hydrogen and chlorine in hydrochloric acid may be demonstrated by passing the dry gas over dioxide of manganese heated to redness, when dichloride of manganese, chlorine, and water are the resulting products.

Distinguishing Tests.—The strong aqueous solution heated with binoxide of manganese yields chlorine. Strong or dilute solutions yield with nitrate of silver a white precipitate insoluble in nitric acid, soluble in ammonia. Distilled with strong sulphuric acid and potassium bichromate, it yields chlorochromic acid. Soluble chlorides give the same reactions, the second only with strong sulphuric acid.

Physiological Action.—Powerfully corrosive and irritant poison. Very destructive to vegetation, even when largely diluted with air.

Preparation—*From sodium chloride by the action of strong sulphuric acid.* The sodium chloride must be fused before use as otherwise much frothing occurs. The acid sulphate of sodium is formed at a moderate heat, thus:—

Sodium Chloride.		Sulphuric Acid.		Acid Sodium Sulphate.		Hydrochloric Acid.
$Na\,Cl$	+	$H_2\,S\,O_4$	=	$Na\,H\,S\,O_4$	+	$H\,Cl$.

At a temperature approaching red heat neutral sodium sulphate is formed, thus:—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The gas may be passed into water kept cool; or, if required dry, must be collected over mercury, after passage over pumice-stone moistened with sulphuric acid or over chloride of calcium.

Other Modes of Production.—Hydrochloric acid gas is formed with explosion when equal volumes of hydrogen and chlorine are ignited, or heated to about 150°, or brought into contact with spongy platinum, or exposed to sunlight or to the light of burning magnesium (see also Chlorine), with evolution of about 22,000 heat units.

Manufacture.—The gas is obtained as a bye-product in the manufacture of sodium sulphate, from sodium chloride and sulphuric acid. The commercial acid contains many impurities, such as sulphuric acid, hlorine, arsenic, iron, &c.

NITRO-HYDROCHLORIC ACID OR AQUA REGIA.

Neither nitric nor hydrochloric acid singly has the power of dissolving gold, which, however, is readily dissolved by a mixture of the two acids, hence the name of this mixture. This power depends chiefly on the formation of chlorine by the mutual action of the acids on each other, particularly when heated together; whereby, however, compounds containing chlorine and nitrogen are also produced; namely, chloronitric acid and chlonitrous acid (nitric and nitrous oxychlorides).

$$HNO_3 + 3HCl = NOCl + 2H_2O + Cl_2,$$
$$2HNO_3 + 6HCl = 2NOCl_2 + 4H_2O + Cl_2.$$

The mixture is used for dissolving gold, platinum, and analogous metals. The best proportion is 1 part of nitric to 3 parts of hydrochloric acids.

HYPOCHLOROUS ANHYDRIDE.

$Cl_2O = 87$. Percentage composition, $O = 18{\cdot}41$; $Cl = 81{\cdot}59$. Gas at ordinary temperatures. Liquid at $-20°$. Specific gravity, $2{\cdot}97$ (air = 1).

Physical Properties.—Under ordinary conditions a yellowish gas of penetrating chlorine-like odour. It is very soluble in water; 1 volume water at 0° absorbs 200 volumes of the gas. At $-20°$ it is condensed to a dark red liquid, which boils at $+20°$, and which is heavier than water.

Chemical Properties.—Hypochlorous anhydride is a very unstable and highly explosive compound, even at ordinary temperatures or in contact with various substances.

Preparation.—By passing dry chlorine over dry precipitated mercuric oxide, which has previously been slightly heated, and cooling the resulting gas to $-20°$.

$$\underset{\text{Mercuric Oxide.}}{HgO} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Mercuric Chloride.}}{HgCl_2} + \underset{\text{Hypochlorous Anhydride.}}{Cl_2O.}$$

HYPOCHLOROUS ACID.

$HClO = 52{\cdot}5$. $[Cl.OH]$. *Percentage composition*, $H = 1{\cdot}92$; $O = 30{\cdot}46$; $Cl = 67{\cdot}62$. *Liquid at ordinary temperatures.*

Physical Properties.—The concentrated acid is a yellowish liquid of a very volatile nature.

Chemical Properties.—This compound, which may be regarded as the hydrate of hypochlorous anhydride (Cl_2O), is a monobasic acid and is fairly stable when dilute, but when concentrated it decomposes spontaneously even in the dark, and rapidly in sunlight, yielding chlorine and chloric or chlorous acid. Heated with excess of hydrochloric acid both hypochlorous acid and its salts yield chlorine (see below).

Its calcium salt constitutes the active principle in bleaching powder. It is a powerful oxidising agent; thus, carbon, iodine, sulphur, phosphorus, arsenic, and antimony become converted by it into carbonic, iodic, sulphuric, &c., acids, sometimes with explosion. It forms a large series of salts known as hypochlorites.

Preparation.—1. By passing chlorine into water containing chalk or freshly-precipitated mercuric oxide in suspension.

$$\underset{\text{Chalk.}}{CaCO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Carbonic Anhydride.}}{CO_2} + \underset{\text{Calcium Chloride.}}{CaCl_2} + \underset{\text{Hypochlorous Acid.}}{2HClO.}$$

$$\underset{\text{Mercuric Oxide.}}{2HgO} + \underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Mercuric Chloride.}}{HgCl_2} + \underset{\text{Hypochlorous Acid.}}{2HClO.}$$

2. By passing hypochlorous anhydride gas into water.

$$\underset{\text{Hypochlorous Anhydride.}}{Cl_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hypochlorous Acid.}}{2HClO.}$$

3. By distillation of bleaching powder with not more than half its equivalent of dilute nitric acid (see below).

BLEACHING POWDER (*Chloride of Lime*).

When chlorine is passed over moist lime at a low temperature, it is absorbed in considerable quantity. The reaction which takes place is often expressed as follows :—

$$\underset{\text{Lime.}}{2CaH_2O_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Calcium Chloride.}}{CaCl_2} + \underset{\text{Calcium Hypochlorite.}}{Ca(ClO)_2} + \underset{\text{Water.}}{2H_2O.}$$

The compound formed is soluble in water, and, if the solution be exposed to a freezing mixture, crystals of calcium hypochlorite [$Ca(ClO)_2, 4H_2O$] are obtained, while calcium chloride remains in solution (Kingzett).

Distilled with excess of dilute nitric or sulphuric acid, bleaching powder yields chlorine, since the hydrochloric and hypochlorous acids at first liberated decompose one another, thus :—

$$\overset{\text{Bleaching Powder.}}{CaCl_2O_2, CaCl_2} + \overset{\text{Sulphuric Acid.}}{2H_2SO_4} = \overset{\text{Calcium Sulphate.}}{2CaSO_4} + \overset{\text{Hypochlorous Acid.}}{2HClO} + \overset{\text{Hydrochloric Acid.}}{2HCl}$$

$$\overset{\text{Hypochlorous Acid.}}{HClO} + \overset{\text{Hydrochloric Acid.}}{HCl} = \overset{\text{Chlorine.}}{Cl_2} + \overset{\text{Water.}}{H_2O}.$$

Bleaching powder appears, however, not to be a true mixture of calcium chloride and hypochlorite, but rather a compound having the formula, $CaOCl_2$, or [$CaCl(OCl)$] (Odling), since, when properly manufactured, it is not deliquescent (while calcium chloride is), and yields very little calcium chloride to alcohol, and all its chlorine is expelled by carbonic acid.

In bleaching, the goods are repeatedly dipped, first in a dilute solution of the bleaching powder, and next in dilute sulphuric acid—chlorine is evolved and exerts its bleaching action (cf. Chlorine, p. 169).

CHLOROUS ANHYDRIDE.

The gas which was supposed to be chlorous anhydride of the composition Cl_2O_3, has been proved to be a mixture of chlorine peroxide and chlorine.

CHLOROUS ACID.

$HClO_2 = 68{\cdot}5$. [$Cl\,O.O\,H$]. *Percentage composition*, $H = 1{\cdot}46$; $O = 46{\cdot}72$; $Cl = 51{\cdot}82$.

This acid is known only in admixture with chloric acid (see chlorine peroxide, p. 177), but has not been isolated; some of its salts are, however, known and are called chlorites; potassium chlorite, $K\,Cl\,O_2$, for example, is formed together with potassium chlorate, $K\,Cl\,O_3$, when potassium hydrate is acted upon by dioxide of chlorine; the two salts can be separated by crystallisation.

Chlorine Dioxide.		Potassium Hydroxide.		Potassium Chlorite.		Potassium Chlorate.		Water.
$2\,Cl\,O_2$	$+$	$2\,K\,H\,O$	$=$	$K\,Cl\,O_2$	$+$	$K\,Cl\,O_3$	$+$	$H_2\,O$

CHLORIC ACID.

$HClO_3 = 84{\cdot}5$. $[Cl\,O_2.OH]$. *Percentage composition*, $H = 1{\cdot}18$ $Cl = 42{\cdot}01$; $O = 56{\cdot}81$.

Physical Properties.—The hydrate is a syrupy, very acid, yellowish, almost odourless liquid.

Chemical Properties.—The hydrate as obtained below is a very unstable compound. It first reddens, then bleaches blue litmus. Heated above 40° it begins to decompose. Brought into contact with paper, linen, &c., it sets fire to them. It is a definite acid, and forms salts (called chlorates), which are stable at ordinary temperatures, but which, at higher temperatures, or in contact with various substances, are decomposed often with explosive violence (see Chlorates).

Preparation—1. *From potassium chlorate by the action of hydrofluosilicic acid.*—If a solution of potassium chlorate is heated with a solution of hydrofluosilicic acid, a precipitate of potassium fluosilicate is formed and chloric acid goes into solution. The liquid is decanted and evaporated under 30°, with addition of finely divided silica to remove the excess of the hydrofluosilicic acid.

$$2\,K\,Cl\,O_3 \quad + \quad H_2\,Si\,F_6 \quad = \quad K_2\,Si\,F_6 \quad + \quad 2\,H\,Cl\,O_3.$$

2. *From barium chlorate by the action of sulphuric acid*, and concentration under the air-pump to a syrup, or on a water-bath at a temperature not exceeding 38°.

CHLORINE DIOXIDE.

(*Chlorine peroxide*) $Cl\,O_2 = 67{\cdot}5$. *Percentage composition*, $0 = 47{\cdot}4$; $Cl = 52{\cdot}6$.

Physical Properties.—This compound is a yellowish red fluid, boiling at about 9°, and giving off a yellow-green gas. Water dissolves twenty times its volume of the gas.

Chemical Properties.—It is extremely unstable. The gas explodes at about 60° with great violence. The fluid is also decomposed with explosion in contact with organic matters. Sunlight also decomposes it. Its composition is very doubtful. It has probably the composition Cl_2O_4 in the fluid state. With water it forms a mixture of hypochlorous and chloric acids—

$$\overset{\text{Chlorine Dioxide.}}{2\,ClO_2} + \overset{\text{Water.}}{H_2O} = \overset{\text{Chlorous Acid.}}{HClO_2} + \overset{\text{Chloric Acid.}}{HClO_3}.$$

With bases it acts in a similar manner.

Many substances, such as phosphorus, sulphur, cane-sugar, &c., are spontaneously inflammable when brought into contact with chlorine peroxide.

Preparation.—By extremely cautious distillation of potassium chlorate and sulphuric acid on a water-bath at a temperature not exceeding 40°.

$$\overset{\text{Potassium Chlorate.}}{3\,KClO_3} + \overset{\text{Sulphuric Acid.}}{H_2SO_4} = \overset{\text{Potassium Perchlorate.}}{KClO_4} + \overset{\text{Potassium Sulphate.}}{K_2SO_4} + \overset{\text{Chlorine Dioxide.}}{Cl_2O_4} + \overset{\text{Water.}}{H_2O}.$$

PERCHLORIC ACID.

$HClO_4 = 100{\cdot}5$. $[ClO_3 . OH]$. Percentage composition, $Cl = 35{\cdot}33$; $H = 0{\cdot}99$; $O = 63{\cdot}68$. Fluid at ordinary temperatures. Freezing point − 38°. Specific gravity at 15·5°, 1·78 (water = 1).

Physical Properties.—Perchloric acid is a colourless oily fluid, resembling sulphuric acid in appearance, of very acid taste and chlorine-like smell. It fumes in air, being very hygroscopic. It cannot be distilled without decomposition; at 75° it becomes darker in colour, the temperature rises rapidly, and explosion may take place. When dropped into water it hisses and causes considerable rise of temperature.

Chemical Properties.—Perchloric acid, though not very stable in the concentrated form, is, when diluted with water, one of the most stable of the oxygen acids of chlorine. The concentrated acid is liable to spontaneous explosion on long exposure to light. It explodes also in contact with charcoal and with organic matters (such as wood, paper, &c., which it ignites). It is miscible with alcohol, but is liable to explode on mixing. With ether it explodes violently. The diluted acid will dissolve certain metals (zinc and iron), with evolution of hydrogen, and does not destroy vegetable colours. The concentrated acid has the formula, $HClO_4$. A crystalline hydrate, $HClO_4 . H_2O$ is also known. It is a monobasic acid, and forms salts called perchlorates.

Preparation.—1. By heating pure potassium perchlorate with four times its weight of strong sulphuric acid.

Potassium Perchlorate.		Sulphuric Acid.		Hydric Potassium Sulphate.		Perchloric Acid.
$KClO_4$	+	H_2SO_4	=	$KHSO_4$	+	$HClO_4$.

NITROGEN TRICHLORIDE—$NCl_3 = 120{\cdot}5$.

Properties.—An oily liquid of a most dangerously explosive character.

Preparation.—By inverting a wide-mouthed bottle of chlorine gas over a solution of ammonium chloride (see also p. 114).

Ammonium Chloride.		Chlorine.		Nitrogen Trichloride.		Hydrochloric Acid.
NH_4Cl	+	$6Cl$	=	NCl_3	+	$4HCl$.

This substance can only be experimented with under the most stringent precautions.

BORON CHLORIDE—$BCl_3 = 117{\cdot}5$.

Specific gravity of liquid, 1·35 (*water* = 1); *of vapour*, 58·75 ($H = 1$). *Boiling point*, 18·2°.

Properties.—A fuming liquid decomposed by water with production of boric and hydrochloric acids.

Preparation.—By the action of dry chlorine on a mixture of boric anhydride and charcoal at a high temperature.

SILICON TETRACHLORIDE—$SiCl_4 = 170$.

Specific gravity of liquid, 1·52 (*water* = 1); *of vapour*, 85 ($H = 1$). *Boiling point*, 59°.

Properties.—A colourless volatile liquid of pungent and irritating odour. Is decomposed by water with formation of silica and hydrochloric acid.

Preparation.—By passing chlorine over a mixture of silica and charcoal at a red heat.

CHLORIDES OF SULPHUR.

Three chlorides of sulphur are known, viz.:—

1. *Disulphur dichloride*, S_2Cl_2. A dark yellowish-red liquid which fumes in air, and possesses an unpleasant and very penetrating odour; specific gravity 1·7, boiling point 138°. It dissolves sulphur easily. It is decomposed by water, with separation of sulphur, and formation of sulphurous anhydride and hydrochloric acid. It is prepared by passing dry chlorine over melted sulphur in a retort.

2. *Sulphur dichloride*, SCl_2. A deep red, very unstable liquid of similar properties to the above, and formed by saturating the above with chlorine at a temperature below 0°.

3. *Sulphur tetrachloride*, SCl_4. A highly unstable, yellowish-red fluid, formed by saturating the disulphur dichloride with chlorine at a temperature below − 20°.

OXYCHLORIDES OF SULPHUR.

The following oxychlorides of sulphur are also known:—

Sulphurous chloride (thionyl chloride), . .	$SOCl_2$.
Sulphuric chloride (sulphuryl chloride, chlorosulphuric acid), ...	SO_2Cl_2.
Pyrosulphuric chloride, ...	$S_2O_5Cl_2$; $[(SO_2Cl)_2O]$.
Sulphuric hydroxychloride, ...	$HClSO_3$; $[SO_2 . HO . Cl]$.

BROMINE.

(*βρῶμος, a stench*) $Br = 80$, $Br_2 = 160$. *Liquid at ordinary temperatures; boiling point*, 59·5°. *Solid at* − 7·05. *Specific gravity of vapour*, 5·39 (*air* = 1); 80 ($H = 1$); *of liquid*, 2·96 *at* 15° (*water* = 1). *Monad to heptad.*

Occurrence in Nature.—Bromine, like chlorine, is not found free in nature, and it belongs to the class of rarer elements. It is chiefly found in sea-water as bromide of magnesium accompanying chlorine, but in very much smaller quantity, and in a very few mineral springs, notably that of Kreuznach, and in the rock-salt deposit at Stassfurt.

Physical Properties.—Bromine is the only element besides mercury which is liquid at ordinary temperatures. The liquid is of an intense, red-brown colour and is extremely volatile, emitting at all temperatures a heavy, deep red-brown vapour, having a quite peculiar, unpleasant, very penetrating and irritating odour, somewhat resembling that of chlorine, but quite distinguishable, and of a sharp and stringent caustic taste. It is slightly soluble in water; 30 parts of water dissolve 1 part bromine at 10°. It is much more freely soluble in alcohol and ether. It is best kept covered with a layer of water. It is an absorbent of heat rays.

Chemical Properties.—Bromine resembles chlorine in its chemical properties in almost every respect, but its action in nearly all cases is less intense. Its vapour supports the combustion of a burning taper. It combines directly with phosphorus and many metals, and has also a special attraction for hydrogen. Its action on ammonia is similar to that of chlorine; it acts as an indirect oxidising agent in the presence of water, and bleaches vegetable-colouring matters in a distinctly analogous manner. Its solution in water (bromine water) also undergoes decomposition analagous to that of chlorine water, and it forms, below 4°, a crystalline hydrate having the formula, $Br_2, 10\,H_2O$.

The direct compounds of bromine are termed bromides.

Distinguishing Tests.—Bromine is a deep red-brown, very volatile liquid of peculiar and very irritating odour; forms an orange-coloured compound with moist starch; liberates iodine from iodide of potassium; is soluble in ether, forming a yellowish-brown solution; bromides yield, with silver salts, a pale yellowish precipitate, insoluble in nitric acid, soluble, though not very readily, in ammonia.

Physiological Action.—Its action on the lungs is similar to, but even more intense than, that of chlorine; it stains the skin yellow, and is a powerful caustic. It is also a disinfectant.

Preparation.—1. *From sodium (or potassium) bromide by the action of dioxide of manganese and sulphuric acid.* The reaction is analogous to the preparation of chlorine (*q.v.*, p. 170), according to the equation—

$$\overset{\substack{\text{Sodium}\\\text{Bromide.}}}{2\,NaBr} + \overset{\substack{\text{Manganese}\\\text{Dioxide.}}}{MnO_2} + \overset{\substack{\text{Sulphuric}\\\text{Acid.}}}{3\,H_2SO_4} = \overset{\substack{\text{Manganese}\\\text{Sulphate.}}}{MnSO_4} + \overset{\substack{\text{Acid}\\\text{Sodium Sulphate.}}}{2\,NaHSO_4} + \overset{\text{Water.}}{2\,H_2O} + \overset{\text{Bromine.}}{Br_2}.$$

2. *Ether Process.*—Balard used the following for extracting bromine from sea water. The mother liquor from sea water or mineral waters is mixed with sufficient amount of chlorine water to liberate all the bromine. The brownish solution is shaken up with ether, which dissolves the liberated bromine, and the ethereal solution is in its turn shaken up with a solution of caustic potash or soda, to which it parts with its bromine, bromide and bromate of potassium or sodium being formed ($3\,Br_2 + 6\,KHO = 5\,KBr + KBrO_3 + 3\,H_2O$). The aqueous solution is evaporated and the dry residue after ignition, which converts the bromate into bromide, distilled with binoxide of manganese and sulphuric acid. The decolourised ether is used for the extraction of fresh quantities of bromine.

Manufacture.—1. Bromine is extracted from the mother liquors of sea or mineral water, by heating the same with dioxide of manganese and sulphuric acid, and condensing the vapour which is evolved.

HYDROBROMIC ACID.

$HBr = 81$. Percentage composition, $H = 1{\cdot}23$, $Br = 98{\cdot}77$. Gas at ordinary temperatures. Specific gravity, 2·71 (air = 1). Liquid at −73°; solid at −87°.

Physical Properties.—Hydrobromic acid is a colourless gas, of peculiar odour. It forms fumes with moist air. It is, like hydrochloric acid, extremely soluble in water. The solution is colourless, very acid, fumes in air, and when saturated has a specific gravity of 1·78. A solution of hydrobromic acid, boiling at 126°, has a specific gravity of 1·486, and contains 47 per cent. of its weight of the gas. Such a solution distils unchanged.

Chemical Properties.—Hydrobromic acid resembles hydrochloric acid chemically in almost every respect, except that it is a weaker acid and that chlorine is able to eject its bromine. It is like hydrochloric acid, a monobasic acid. Its salts are called bromides.

Distinguishing Tests.—If chlorine water be added in small quantity to hydrobromic acid, or to a solution of a bromide, bromine is ejected and may be dissolved on addition of ether or bisulphide of carbon which it colours yellow. Nitrate of silver yields, with the acid or its salts in solution, a pale yellow precipitate insoluble in nitric acid, difficultly soluble in ammonia.

Physiological Action.—Potassium bromide is a powerful alterative in nervous and other diseases.

Preparation.—Hydrobomic acid cannot be prepared by the action of sulphuric acid upon a bromide, owing to the simultaneous production of bromine which occurs, but may be prepared by using phosphoric acid. Other methods are, however, generally resorted to, viz.:—

1. *By the action of water on phosphorus tribromide.*—Water and red phosphorus are placed in a retort, and bromine is brought gradually into contact with them by means of a separating funnel passing through the neck of the retort. Somewhat violent action ensues, tribromide of phosphorus being formed, which in contact with water yields phosphorous and hydrobromic acids respectively.

$$\overset{\text{Phosphorus Tribromide.}}{PBr_3} + \overset{\text{Water.}}{3H_2O} = \overset{\text{Phosphorous Acid.}}{H_3PO_3} + \overset{\text{Hydrobromic Acid.}}{3HBr.}$$

The latter coming over in the form of vapour may be collected over mercury after drying, or may be passed into water if a solution is required.

2. *By passing sulphuretted hydrogen through bromine water.*

$$\overset{\text{Hydrogen Sulphide.}}{H_2S} + \overset{\text{Bromine.}}{Br_2} = \overset{\text{Hydrobromic Acid.}}{2HBr} + \overset{\text{Sulphur.}}{S.}$$

Sulphur is deposited, and the hydrobomic acid formed goes at once into solution.

OXYGEN ACIDS OF BROMINE.

Hypobromous acid, ...	$HBrO.$
Bromic acid, ...	$HBrO_3.$
Perbromic acid, ...	$HBrO_4.$

These substances, of which bromic acid is the best known, may be obtained in a strictly analogous manner to the corresponding chlorine compounds and possess very similar properties.

Sodium Hypobromite.—A strongly alkaline solution of hypobromite of sodium prepared by dissolving 2·2 c.c. bromine in 23 c.c. caustic soda solution (containing 1 part of soda to 2½ parts water) is now frequently used in the estimation of *urea* [$CO(NH_2)_2$] in urine. The following reaction occurs:—

$$\overset{\text{Urea.}}{CON_2H_4} + \overset{\text{Sodium Hypobromite.}}{3NaBrO} + \overset{\text{Soda.}}{2NaHO} = \overset{\text{Nitrogen.}}{N_2} + \overset{\text{Sodium Bromide.}}{3NaBr} + \overset{\text{Sodium Carbonate.}}{Na_2CO_3} + \overset{\text{Water.}}{3H_2O.}$$

The nitrogen is collected, and forms a measure of the urea present in the urine examined The solution of sodium hypobromite is very unstable, even at ordinary temperatures, being gradually converted into bromide and bromate, $3NaBrO = 2NaBr + NaBrO_3$ — and can then no longer be used.

IODINE.

(*ἰώδης, violet coloured*)—$I = 127$, $I = 254$. *Solid at ordinary temperatures; melting point*, 107°; *boiling point*, 180°. *Specific gravity of solid*, 4·95 (*water* = 1); *of vapour*, 8·65; (*air* = 1), 127 ($H = 1$). [*At very high temperatures*, 84·66 ($H=1$)]. *Monad. Specific heat*, 0·0541.

Occurrence in Nature.—Iodine is not found free in nature, and, like bromine, belongs to the class of rarer elements. It occurs (chiefly as iodates) in minute traces in sea water, from which it is absorbed by sea-weeds, and in Chili saltpetre, the mother-liquors from the crystallisation of which constitute one of the chief sources from which it is obtained. It is also found in a few mineral springs, and in some rarer minerals. In very minute traces it is very widely diffused in most spring waters, in the air, &c.

Physical Properties.—At all ordinary temperatures iodine is a gray-black soft solid, having an almost metallic lustre and crystalline structure (rhombic octahedra). It is very volatile, emitting even at ordinary temperatures a violet vapour of peculiar odour, resembling somewhat that of Cl and Br, and can be sublimed at a temperature considerably below its melting point. If sublimed slowly, well-formed crystals may be obtained. Its vapour is of a fine violet colour; hence the name of the element. It is very slightly soluble in water—one part of iodine requiring 7,000 parts water, to which it imparts a yellowish tint. It is, however, soluble to a considerable extent in water, containing potassium iodide (or some other salts), and freely soluble in alcohol, ether, chloroform, and bisulphide of carbon—in the former, with a brownish colour, in the two last with a beautiful and intense rose or pink colour. It is a non-conductor of electricity. A strong solution of iodine in bisulphide of carbon is opaque to light, but allows the obscure heat rays to pass almost unchecked; (diathermous).

Chemical Properties.—Iodine closely resembles chlorine and bromine in most of its chemical properties—thus, it unites directly with phosphorus, sulphur, iron, zinc, &c. The pure aqueous solution does not bleach. No hydrate of iodine is known. It is ejected from its combinations with hydrogen and the metals by chlorine and bromine. On the other hand, it ejects chlorine and bromine from their oxygen compounds.

Distinguishing Tests.—Iodine may be distinguished from all other substances, as a gray-black crystalline opaque solid, subliming at comparatively low temperature, emitting a violet vapour which yields a deep blue colouration with moist starch. This last is a very delicate reaction. It dissolves in chloroform or bisulphide of carbon with an intense rose or pink colour, which forms, perhaps, the most delicate test for iodine.

Physiological Action.—Applied externally in the form of a solution, iodine acts as an irritant and caustic; taken internally, it acts locally as an irritant, and produces catarrh of the mucous membranes generally. It stains the skin transiently yellow, and destroys it on repeated application. It acts as a stimulant of the absorbent glands and capillary circulation. Considerable differences exist in the susceptibility of different constitutions to the action of iodine. It is a powerful disinfectant.

Preparation—1. *From commercial iodine.*—Pure iodine for laboratory purposes is easily prepared from commercial iodine by sublimation, and the process can be repeated if necessary.

2. By dissolving commercial iodine in boiling alcohol, and filtering the hot solution into a large quantity of water, pure iodine is precipitated.

3. *From iodide of potassium by the action of dioxide of manganese and sulphuric acid.*—This reaction is analogous to preparation of bromine from bromide of potassium, and of chlorine from chloride of potassium, and needs no further explanation.

$$\overset{\substack{\text{Sodium}\\\text{Iodide.}}}{2NaI} + \overset{\substack{\text{Manganese}\\\text{Dioxide.}}}{MnO_2} + \overset{\substack{\text{Sulphuric}\\\text{Acid.}}}{3H_2SO_4} = \overset{\substack{\text{Manganese}\\\text{Sulphate.}}}{MnSO_4} + \overset{\substack{\text{Acid-Sodium}\\\text{Sulphate}}}{2NaHSO_4} + \overset{\text{Water.}}{2H_2O} + \overset{\text{Iodine.}}{I_2}.$$

The iodine vapour may be condensed in the neck of the retort or in suitable receivers. The reaction is more especially interesting as illustrating its manufacture.

Manufacture.—Iodine is manufactured from the ashes of sea-weed collected on the Coast of Scotland and Normandy, and known as *kelp* and *varec* respectively, in which it is present in combination with potassium, sodium, and magnesium. These salts, being very soluble, are after extraction of the ash with water and concentration, retained in the mother-liquor, through which chlorine gas is passed, excess being avoided, when the iodine separates out in the form of a fine black precipitate. This is collected and refined by sublimation.

Or the concentrated mother-liquor, after being mixed with sulphuric acid of specific gravity 1·7, is let stand for twenty-four hours (when sulphate of soda crystallises out), and the clear liquor, after being drawn off, is mixed with dioxide of manganese and strong sulphuric acid, and subjected to distillation, the iodine being condensed in specially constructed globular receivers. Considerable quantities are now obtained from the mother-liquors after the crystallisation of Chili saltpetre, by similar processes.

HYDRIODIC ACID.

HI = 128. Percentage composition, H = 0·78, I = 99·22. Gas at ordinary temperatures. Specific gravity, 4·44 *(air* = 1); 64 (H = 1), *easily liquefied by pressure; solid at* – 55°. 11·19 *litres weigh* 64 *grammes.*

Physical Properties.—Hydriodic acid is a colourless gas of peculiar odour, which forms a cloud with moist air. It is extremely soluble in water. The solution is colourless, very acid, fumes in air, and when saturated has a specific gravity of 2·0. A solution of hydriodic acid of specific gravity 1·7 has a constant boiling point of 126°, and contains 57 per cent. of its weight of the gas.

Chemical Properties.—Hydriodic acid is a very unstable compound, and in presence of oxygen yields water and free iodine. It resembles hydrochloric and hydrobromic acids in its properties, but is a much weaker acid; its iodine is ejected by chlorine and bromine. It has the property of dissolving iodine very readily. It is a monobasic acid. Its salts are called iodides.

Distinguishing Tests.—Chlorine- or bromine-water, nitrous acid, &c., liberate iodine from an iodide, which may be further confirmed by dissolving the free iodine in chloroform, with which it gives a pink solution, or by adding a solution of starch, in which it produces an intense blue coloration. With nitrate of silver iodides give a yellowish precipitate insoluble both in acid and in ammonia.

Hydriodic acid and solutions of iodides yield a black precipitate with chloride of palladium, and a yellowish precipitate with silver salts insoluble both in nitric acid and in ammonia, but turned white by the latter.

Physiological Action.—Potassium iodide is a powerful alterative and is much used in medicine.

Preparation.—The same remarks apply here as in the case of hydrobromic acid (see p. 181).

1. *By the action of water on phosphorous tri-iodide.* If amorphous phosphorus and iodine are gently heated in a tube with a little water, tri-iodide of phosphorus is formed, which, with the water, yields phosphorous and hydriodic acids respectively—

$$\underset{\text{Tri-iodide.}}{\overset{\text{Phosphorous}}{PI_3}} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Acid.}}{\overset{\text{Phosphorous}}{H_3PO_3}} + \underset{\text{Acid.}}{\overset{\text{Hydriodic}}{3HI.}}$$

The latter may be collected, after drying, over mercury, or passed into water if a solution is required.

2. *By passing sulphuretted hydrogen through water in which iodine is suspended—*

Hydrogen Sulphide.		Iodine.		Hydriodic Acid.		Sulphur.
H_2S	+	I_2	=	$2HI$	+	S.

Sulphur is deposited, and the hydriodic acid formed goes at once into solution.

IODIC ANHYDRIDE—$I_2O_5 = 334$.

Properties.—A white solid, which, on strongly heating, is decomposed into iodine and oxygen.

Preparation.—From iodic acid by heating to 107° (see below).

OXYGEN ACIDS OF IODINE.

Of these the following two only are well known:—iodic acid, HIO_3, and periodic acid, HIO_4.

IODIC ACID.

$HIO_3 = 176$. Percentage composition, $H = 0{\cdot}57$, $O = 27{\cdot}27$, $I = 72{\cdot}16$. Solid at ordinary temperatures. Specific gravity, 4·62 (water = 1).

Physical Properties.—Iodic acid crystallises in white rhombic crystals, which are very soluble in water.

Chemical Properties.—Iodic acid is a comparatively stable compound, differing greatly in this respect from the corresponding chlorine and bromine compounds. At 107° it loses water and is converted into the anhydride ($2HIO_3 - H_2O = I_2O_5$). Neither chlorine nor bromine have any action upon it. Sulphurous acid, phosphorous acid, nitrous acid, sulphuretted hydrogen, and other reducing agents liberate iodine from a solution of iodic acid. Hydriodic and iodic acids mutually decompose each other with formation of water and separation of iodine:—$5HI + HIO_3 = 3H_2O + 3I_2$. It is a monobasic acid. Its salts are called iodates, and these compounds closely resemble chlorates and bromates.

Distinguishing Tests.—It yields iodine (recognised by its action on starch or chloroform), when acted on by reducing agents.

Preparation.—*By the action of nitric acid upon iodine.* The iodine is oxidised to iodic acid, which, not being very soluble in nitric acid, separates out as a crystalline powder, and may be purified by recrystallisation.

2. *By decomposition of barium iodate with dilute sulphuric acid.*

PERIODIC ACID.

$HIO_4 = 192$. *Percentage composition*, $H = 0{\cdot}52$, $O = 33{\cdot}34$, $I = 66{\cdot}14$.

Physical Properties.—Normal periodic acid has not yet been prepared. The acid crystallises from the solution in colourless deliquescent crystals which melt between 130° and 136°, and have the composition, $HIO_4, 2H_2O$.

Chemical Properties.—Forms a series of extremely complex salts, the constitution of which is most readily explained on the assumption that iodine is a heptad. Is reduced with liberation of iodine by the action of dilute sulphuric acid and zinc, and by sulphuretted hydrogen, but not by sulphurous or nitrous acid. It is slowly decomposed a little above its melting point into iodic anhydride, oxygen, and water.

Distinguishing Tests.—Yields iodine with zinc and sulphuric acid, but not with sulphurous acid.

Preparation.—1. *By the action of iodine on perchloric acid.*

$$\begin{array}{ccccccc} \text{Perchloric Acid.} & & \text{Iodine.} & & \text{Periodic Acid.} & & \text{Chlorine.} \\ 2HClO_4 & + & I_2 & = & 2HIO_4 & + & Cl_2. \end{array}$$

2. By passing chlorine into a solution containing iodate of soda and sodium hydroxide, a sparingly soluble basic periodate of sodium is formed, which is dissolved in dilute nitric acid and precipitated with acetate of lead, periodate of lead is thrown down, and is decomposed by means of dilute sulphuric acid.

3. *By boiling periodate of silver with water*, when it breaks up into an insoluble basic salt and periodic acid.

NITROGEN IODIDE—$NI_3 = 395$.

When powdered iodine is digested for some time with strong ammonia solution and the mixture is stirred with a feather and filtered, a black residue is left upon the filter, which, after washing with alcohol and drying in small portions by exposure to the air on filter-paper, explodes with considerable violence, even at the touch of a feather. Its composition is not definitely determined, and it probably contains hydrogen. Great care is necessary in handling the dry material, and very small quantities only should be dealt with at one time.

CHLORIDES OF IODINE.

Two chlorides of iodine are known, their formulæ being respectively ICl and ICl_3.

FLUORINE.

(*Fluo, I flow*)—*gas at ordinary temperatures*, $F = 19$. *Monad.*

Occurrence in Nature.—Fluorine does not occur in nature in the free state, and has only recently been known in the elementary condition. It is found chiefly in combination with calcium as *fluorspar*, $Ca\,F_2$, and as *cryolite*, $3\,Na\,F, Al\,F_3$. As fluoride of calcium it is very widely diffused, and is present in the bones and in the enamel of the teeth, and in minute traces in almost all natural waters.

Physical Properties.—A colourless gas.

Chemical Properties.—Fluorine has intense combining powers, even at ordinary temperatures, uniting directly with many elements with evolution of much heat and light. With hydrogen it unites explosively, even in the dark.

Preparation.—Anhydrous hydrofluoric acid, in which some fluoride of potassium has been dissolved to render it capable of conducting electricity, is decomposed by an electric current, when it breaks up into fluorine and hydrogen. The apparatus consists of a U tube of platinum, with stoppers of fluorspar, so as to enable the operator to see into it, and is so arranged that the two gases are collected separately; the two poles of the battery dip into the two limbs respectively, care being taken to prevent the two gases from coming into contact.

HYDROFLUORIC ACID.

$HF = 20$. *Percentage composition*, $F = 95{\cdot}0$, $H = 5{\cdot}0$. *Gas at ordinary temperatures. Specific gravity*, 0·9879 *at* 12·7° (*water* = 1).

Occurrence in Nature.—(See Fluorine.)

Physical Properties.—Hydrofluoric acid is at ordinary temperatures a colourless, irritating gas, which fumes in contact with air, and which, on cooling to a low temperature, is condensed to a mobile and very volatile fluid boiling at about 19·4°.

It is very soluble in water, forming a very acid solution which boils at 120°, has a specific gravity of 1·21, and contains about 35 per cent. of its weight of the gas.

Chemical Properties.—Its most remarkable property is that of dissolving silicates; hence its use for etching on glass and in the analysis of silicates. Owing to this property, it has to be kept in bottles of gutta-percha, lead, or silver. Diluted hydrofluoric acid gradually dissolves most metals (except lead, mercury, and the noble metals). It is a monobasic acid. Its salts are called fluorides. Its action on glass is due to the formation of tetrafluoride of silicon (see Silica, p. 152). $4\,H\,F + Si\,O_2 = Si\,F_4 + 2\,H_2\,O$.

Distinguishing Tests.—The acid, in the form of gas or in solution, etches glass. Fluorides evolve the acid when acted on by strong sulphuric acid.

Physiological Action.—Its vapours are highly irritating and very poisonous. The concentrated solution produces serious sores when brought into contact with the skin, and even the diluted acid must be used with great caution.

Preparation—1. *By the action of sulphuric acid on fluor-spar* (in platinum, or lead retorts).

$$\begin{array}{ccccccc} \text{Calcium Fluoride.} & & \text{Sulphuric Acid.} & & \text{Calcium Sulphate.} & & \text{Hydrofluoric Acid.} \\ CaF_2 & + & H_2SO_4 & = & CaSO_4 & + & 2HF. \end{array}$$

SILICON TETRAFLUORIDE—$SiF_4 = 104$.

Gas at ordinary temperatures; liquid at — 105° under 9 atmospheres pressure. Specific gravity, 3·754 (*air* = 1); 52 ($H = 1$).

Properties.—A colourless, pungent gas, which fumes in contact with air, and is absorbed in great quantity by water with formation of hydrated silica and hydrofluosilicic acid (p. 152).

Preparation and Formation.—See Preparation 1 of Silica, p. 152. It may be collected over mercury. It is this compound which is produced by the action of hydrofluoric acid on silica or silicates.

HYDROFLUOSILICIC ACID—$H_2SiF_6 = 144$. [SiF_4, $2HF$.]

Properties.—This substance is only known in solution. The solution has an acid reaction, and, on evaporation, decomposes, yielding silicon tetrafluoride (SiF_4) and hydrofluoric acid (HF). The acid is dibasic and forms definite salts. It is a useful reagent, and is employed in the preparation of various substances on account of the insolubility of its barium salt ($BaSiF_6$) and of its potassium salt (K_2SiF_6).

Preparation.—*By passing silicon tetrafluoride into water.* See Preparation 1 of Silica, p. 152.

PHOSPHORUS.

(φῶς, *light;* φόρος, *bearer*)—$P = 31$; $P_4 = 124$.[*] *Solid at ordinary temperatures; melting point*, 44°; *boiling point*, 290°; *specific gravity of ordinary solid*, 1·826; *of red*, 2·10 (*water* = 1); *of vapour*, 4·294 (*air* = 1); 62 ($H = 1$). *Triad to pentad.*

Occurrence in Nature.—Owing to its intense attraction for oxygen, phosphorus cannot exist in the elementary form in nature, but is found in considerable quantities, and very widely diffused, in the form of phosphates of the alkali metals, and of the alkaline earths in the mineral, vegetable, and animal kingdoms, and forms as tricalcic phosphate, the chief constituent of bones.

It constitutes in combination with complex organic radicals, a normal

[*] See p. 62.

constituent of the brain; as phosphates of the alkalies, &c., it occurs in the urine.

Physical Properties.—Phosphorus, like carbon, sulphur, &c., exhibits the phenomenon of *allotropy* in a remarkable degree.

1. *Ordinary Phosphorus.*—At ordinary temperatures it is, when freshly prepared, a light yellow, soft, translucent, wax-like solid of a peculiar garlic-like odour. It is brittle at lower temperatures. It fumes in moist air and gives off a vapour which is luminous in the dark.* It melts at 44°, and when heated to 290° (without access of air) boils, and is converted into a colourless highly inflammable vapour. If distilled with water some phosphorus vapour is carried over with the steam, and on this fact is based a method of detecting its presence in cases of poisoning, the vapour being luminous. Its *specific heat* between 36° and 13° = 0·202 (Kopp).

It is insoluble in water, slightly soluble in alcohol, in ether, in fixed and essential oils, and is very soluble in bisulphide of carbon; it is also dissolved, but with oxidation and conversion into phosphoric acid, by nitric acid and *aqua regia.*

It may be obtained in colourless, transparent, highly refractive crystals belonging to the regular system when deposited from its solutions (dodecahedra and octahedra). When exposed to light for a length of time, or when heated in an atmosphere of nitrogen or of carbonic anhydride to 260° for forty-eight or sixty hours, or in vacuum tubes above 300°, it is converted into the red variety described below, with much evolution of heat.

Phosphorus, both solid and melted, is a non-conductor of electricity (Faraday).

The spectrum of phosphorus contains two green lines, one of which coincides with one of the lines of barium. It imparts a green tinge to the hydrogen flame.

Amorphous Phosphorus.—This modification of phosphorus is a powder (sometimes crystalline) of a deep red colour and of higher specific gravity (2·106) and less specific heat (0·1698) than ordinary phosphorus. It does not shine in the dark, is not ignited by friction, remains unaltered when exposed to the air, and must be heated to 260° in air before it ignites, being previously converted into ordinary phosphorus, and is insoluble in the solvents of ordinary phosphorus, including bisulphide of carbon. Heated out of contact with air to 260° it is converted *without change of weight* into ordinary phosphorus.

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* Oil of turpentine, ether, and ammonia vapour prevent its luminosity and oxidation. It is not luminous in absolutely dry oxygen at ordinary pressures.

Chemical Properties.—Phosphorus in all its forms is a very active element possessing great powers of combination. Ordinary yellow phosphorus is highly inflammable, taking fire a little above its melting point and burning with considerable evolution of heat and formation of white fumes of phosphoric anhydride (P_2O_5). When ignited and introduced into pure oxygen it burns with dazzling brilliancy, forming the same compound.

Exposed to the air, it is rapidly oxidised, and when in large pieces, or very finely divided, or under conditions otherwise favourable to the retention of heat, it takes fire more or less rapidly. Hence it must be kept out of contact with air, and is generally stored under water.

It can readily be ignited by friction, or, if finely divided, will take fire spontaneously; for instance, its solution in bisulphide of carbon, when poured upon filter paper, evaporates, and the residual finely divided phosphorus ignites immediately. Its attraction for oxygen is so great that it will even combine with it under water. If phosphorus is placed in water of a temperature a little above its melting point, and oxygen conducted by means of a brass or iron tube into the melted mass, ignition takes place immediately.

If exposed to moist air it is gradually converted into a solution of phosphoric and phosphorous acids.

When partially covered with water it induces the formation of ozone and peroxide of hydrogen. It combines with chlorine and bromine with evolution of light and heat.

It combines also with sulphur and iodine.

When boiled with solutions of caustic alkalies or alkaline earths it yields hypophosphites and phosphoretted hydrogen, (*q.v.* p. 196).

$$\overset{\text{Phosphorus.}}{P_4} + \overset{\substack{\text{Potassium}\\ \text{Hydrate.}}}{3KHO} + \overset{\text{Water.}}{3H_2O} = \overset{\substack{\text{Potassium}\\ \text{Hypophosphite.}}}{3KH_2PO_2} + \overset{\substack{\text{Phosphoretted}\\ \text{Hydrogen.}}}{PH_3}.$$

Owing to its attraction for oxygen it has a powerful reducing action on many salts.

Solutions of salts of silver, gold, platinum, &c., are slowly reduced with deposition of their metals when placed in contact with phosphorus. Gold may in this way be reduced to so fine a state of division that the liquid in which it is suspended appears perfectly clear by transmitted light, showing a magnificent red or blue colour, according to the state of division or fineness of the particles, but appears turbid by reflected light.

The red or amorphous modification above described (see Physical Properties) is, as already stated, much less inflammable than the ordinary phosphorus, requiring to be heated to 260° before it ignites, when it is converted into ordinary phosphorus and burns to phosphoric anhydride. It combines, however, at ordinary temperatures with chlorine, bromine, and iodine, and, when mixed with potassium chlorate, or dioxide of manganese, and some other substances, it readily ignites, even under very slight friction, giving rise to a very violent explosion.

Distinguishing Tests—*Ordinary Phosphorus.*—A soft, waxy solid, which must be kept out of contact with air, owing to its ready inflammability. Exposed to air it gives out white fumes which are luminous in the dark. Distilled with water it yields a distillate which is luminous in the dark when shaken up with air. Boiled with nitric acid it is converted into phosphoric acid.

Amorphous Phosphorus.—A red powder, unaltered in contact with air at ordinary temperatures, but converted into ordinary phosphorus on strongly heating. Boiled with nitric acid, it is converted into phosphoric acid.

Physiological Action.—*Ordinary phosphorus* is a virulent poison, producing fatal effects in doses of one grain and upwards. Persons exposed to its vapour, even at ordinary temperature, such as those engaged in lucifer match manufacture, are liable to *necrosis* of the jaw, particularly in the case of persons previously afflicted with carious teeth, bronchitis, &c. In small doses it is a powerful tonic in various nervous disorders.

Amorphous phosphorus, on the contrary, is non-poisonous when taken internally, and has no effect on persons employed in manufactories where it is used.

Manufacture.—Phosphorus is obtained from calcined bones. The white ash left after the calcination consists chiefly of tricalcic phosphate ($Ca_3\,2\,PO_4$). This is heated with about two-thirds its weight of strong sulphuric acid. In this way calcium sulphate and phosphoric acid are formed.

$$\overset{\text{Tricalcic Phosphate.}}{Ca_3\,2\,PO_4} + \overset{\text{Sulphuric Acid.}}{3\,H_2SO_4} = \overset{\text{Phosphoric Acid.}}{2\,H_3PO_4} + \overset{\text{Calcium Sulphate.}}{3\,CaSO_4}$$

The calcium sulphate is separated by filtration through linen, and the liquid containing the phosphoric acid, after being mixed with charcoal, is evaporated in leaden pans to near dryness and the mass finally heated to redness in stoneware or iron retorts, the necks of which dip into water. The first effect of heating is to expel water and to convert the phosphoric acid into metaphosphoric acid.

Phosphoric Acid.		Water.		Metaphosphoric Acid.
$2H_3PO_4$	$-$	$2H_2O$	$=$	$2HPO_3$

On further heating, the phosphorus of the metaphosphoric acid distils over, carbon monoxide and hydrogen being given off at the same time, thus:—

Metaphosphoric Acid.		Carbon.		Hydrogen.		Carbonic Oxide.		Phosphorus.
$4HPO_3$	$+$	$12C$	$=$	$2H_2$	$+$	$12CO$	$+$	P_4

The crude phosphorus is purified by redistillation, or by melting under water and straining through wash-leather, and is finally cast into sticks which, when cooled rapidly, are at first perfectly transparent, but afterwards become coated with a white covering. When cooled slowly, they are only translucent.

Preparation of Red or Amorphous Phosphorus.—By heating ordinary phosphorus slowly between 240° and 250°, or rapidly at 300°, or by heating phosphorus to 200° with the addition of a minute quantity of iodine, air being excluded.

PHOSPHORIC ANHYDRIDE.

$P_2O_5 = 142$. *Percentage composition,* $P = 43{\cdot}66$; $O = 55{\cdot}34$.

A white, snow-like powder, very deliquescent, and hissing when thrown into water, with which it forms metaphosphoric acid chiefly, thus:—

Phosphoric Anhydride.		Water.		Metaphosphoric Acid.
P_2O_5	$+$	H_2O	$=$	$2HPO_3$.

Preparation.—*By burning phosphorus in oxygen or dry air.*

Phosphorus.		Oxygen.		Phosphoric Anhydride.
P_2	$+$	O_5	$=$	P_2O_5.

HYDRATES OF PHOSPHORIC ANHYDRIDE.

(*Phosphoric Acids.*)

The affinity of phosphoric anhydride for water is even greater than that of sulphuric acid. It forms three hydrates, as enumerated below, but the first and last only can be directly formed, the other being produced by abstraction of water from ordinary phosphoric acid.

$P_2O_5, H_2O = 2HPO_3$	Metaphosphoric acid.
$P_2O_5, 2H_2O = H_4P_2O_7$	Pyrophosphoric acid.
$P_2O_5, 3H_2O = 2H_3PO_4$	Ordinary phosphoric acid.

Solutions of metaphosphoric and pyrophosphoric acid become gradually converted into ordinary phosphoric acid, the change being accelerated by boiling.

Of these three acids the ordinary acid (H_3PO_4) is tribasic, pyrophosphoric acid ($H_4P_2O_7$) is tetrabasic, metaphosphoric acid (HPO_3) is monobasic.

We may now consider each of them separately.

PHOSPHORIC ACID.

(*Tribasic phosphoric acid, orthophosphoric acid*), $H_3PO_4 = 98$. [$PO.(OH)_3$]. *Percentage composition*, $H = 3{\cdot}06$; $P = 31{\cdot}63$; $O = 65{\cdot}31$.

Physical Properties. — Orthophosphoric acid in its most concentrated state forms a syrupy, very acid liquid, of specific gravity 1·85, from which crystals having the formula, H_3PO_4, may be obtained. These are deliquescent and extremely soluble in water.

Chemical Properties.—It is a tribasic acid, and forms, with the metals of the alkalies, three well-defined series of salts which (if M represent an alkali metal) have the following typical formulæ:—(1) MH_2PO_4, (2) M_2HPO_4, (3) M_3PO_4.

Thus, with sodium it forms sodic dihydric phosphate, NaH_2PO_4, disodic hydric phosphate, Na_2HPO_4, trisodic phosphate, Na_3PO_4. Its hydrogen is similarly replaceable by any monad metal, or by any metal of higher valency; thus, tri-argentic phosphate, $Ag_3'PO_4$, triplumbic phosphate, $Pb_3''(PO_4)_2$, ferric phosphate, $Fe'''PO_4$, &c.

If it is heated to 220°, two molecules of the acid lose one molecule of water, and pyrophosphoric acid is formed, thus:—

$$\underset{\text{Tribasic Phosphoric Acid.}}{2H_3PO_4} - \underset{\text{Water.}}{H_2O} = \underset{\text{Pyrophosphoric Acid.}}{H_4P_2O_7}.$$

Heated to redness, one molecule of the acid loses one molecule of water, with formation of metaphosphoric acid, thus:—

$$\underset{\text{Tribasic Phosphoric Acid.}}{H_3PO_4} - \underset{\text{Water.}}{H_2O} = \underset{\text{Metaphosphoric Acid.}}{HPO_3}.$$

Distinguishing Tests.—(See p. 195).

Preparation.—*By oxidising phosphorus with nitric acid.* If phosphorus is dissolved gradually in nitric acid, and the solution evaporated to drive off the excess of acid at a temperature not exceeding 200°, solution of ordinary tribasic phosphoric acid remains.

PYROPHOSPHORIC ACID.

(*Diphosphoric acid*) $H_4 P_2 O_7 = 178$. $[(P\,O)_2\,O\,.\,(O\,H)_4]$. *Percentage composition*, $H = 2{\cdot}24$; $P = 34{\cdot}83$; $O = 62{\cdot}93$.

Physical Properties.—Pyrophosphoric acid is a syrupy, very acid liquid, with difficulty obtained crystalline; it is very soluble in water.

Chemical Properties.—As already stated, a solution of pyrophosphoric acid is converted by boiling into ordinary phosphoric acid.

$$\begin{array}{ccccc} \text{Pyrophosphoric Acid.} & & \text{Water.} & & \text{Tribasic Phosphoric Acid.} \\ H_4\,P_2\,O_7 & + & H_2\,O & = & 2\,H_3\,P\,O_4 \end{array}$$

It is a tetrabasic acid, and forms with monad metals four series of salts.

Distinguishing Tests.—(See p. 195).

Preparation.—1. By heating disodic hydric phosphate, dissolving the residual salt, precipitating with lead acetate, and decomposing the pyrophosphate of lead with sulphuretted hydrogen. 2. By heating ordinary phosphoric acid to 220°.

$$\begin{array}{ccccc} \text{Phosphoric Acid.} & & \text{Water.} & & \text{Pyrophosphoric Acid.} \\ 2\,H_3\,P\,O_4 & - & H_2\,O & = & H_4\,P_2\,O_7. \end{array}$$

METAPHOSPHORIC ACID.

(*Glacial phosphoric acid*, *Monobasic phosphoric acid*) $H\,P\,O_3 = 80$. $[P\,O_2\,.\,O\,H]$. *Percentage composition*, $H = 1{\cdot}25$; $P = 38{\cdot}75$; $O = 60{\cdot}00$.

Physical Properties—A glassy, transparent, amorphous solid, very deliquescent, very soluble in water.

Chemical Properties.—This acid is a monobasic acid, and forms, therefore, only one series of salts. Its solution is gradually converted by boiling into ordinary phosphoric acid.

$$\begin{array}{ccccc} \text{Metaphosphoric Acid.} & & \text{Water.} & & \text{Tribasic Phosphoric Acid.} \\ H\,P\,O_3 & + & H_2\,O & = & H_3\,P\,O_4. \end{array}$$

Preparation.—1. By dissolving phosphoric anhydride in small portions in cold water. 2. By heating ordinary tribasic phosphoric acid to redness.

$$\begin{array}{ccccc} \text{Tribasic Phosphoric Acid.} & & \text{Water.} & & \text{Metaphosphoric Acid.} \\ H_3\,P\,O_4 & - & H_2\,O & = & H\,P\,O_3. \end{array}$$

Distinguishing Tests of the Three Phosphoric Acids—1. *Ordinary Phosphoric Acid.*—When partly or wholly neutralised, a solution of this acid gives a white precipitate with *barium chloride*, soluble in hydrochloric acid, and a yellow precipitate with *silver nitrate;* with *uranium salts* a yellow precipitate insoluble in acetic acid; with *ammonium molybdate* solution, to which strong nitric acid has been added, a yellow precipitate on warming; and with a solution of *magnesium sulphate*, to which *ammonium chloride and ammonia* has been added, a white crystalline precipitate. Neither the acid nor any salt of it coagulates albumen.

2. *Pyrophosphoric Acid.*—A solution of this acid does not coagulate albumen, and, unless neutralised, gives no white precipitate with *barium chloride* or *silver nitrate.*

3. *Metaphosphoric Acid.*—A solution of this acid *coagulates albumen*, and gives a white precipitate with *barium chloride* or *silver nitrate.* Solutions of its salts give the same reactions, but only coagulate albumen on addition of acetic acid.

PHOSPHOROUS ANHYDRIDE.

$P_2O_3 = 110$. *Percentage composition*, $O = 43{\cdot}63$, $P = 56{\cdot}37$.

Properties.—A white, very deliquescent powder of peculiar odour, eagerly attracting oxygen, and sometimes spontaneously inflammable in contact with air, with formation of phosphoric acid. With water it forms phosphorous acid.

$$P_2O_3 + 3\,H_2O = 2\,H_3PO_3.$$

Preparation.—By the slow oxidation of phosphorus with a limited supply of dry air.

PHOSPHOROUS ACID.

$H_3PO_3 = 82$. $[HPO\,.\,(OH)_2]$. *Percentage composition*, $H = 3{\cdot}66$; $P = 37{\cdot}81$; $O = 58{\cdot}54$.

Properties.—A syrupy liquid, from which crystals may be obtained, very deliquescent, and easily oxidisable into ordinary phosphoric acid. When strongly heated it breaks up into phosphoretted hydrogen and ordinary phosphoric acid—

$$4\,H_3PO_3 = 3\,H_3PO_4 + PH_3.$$

It is a very powerful reducing agent; producing a precipitate of silver or mercury, but not of copper, in solutions of salts of these metals. It is a dibasic acid, containing 3 atoms of hydrogen in its molecule but only two hydroxyl groups.

Preparation.—By the action of water on phosphorus trichloride—

$$P\,Cl_3 + 3\,H_2O = H_3PO_3 + 3\,H\,Cl.$$

The hydrochloric acid is expelled on evaporation.

HYPOPHOSPHOROUS ACID.

$H_3PO_2 = 66$. $[H_2PO.OH]$. *Percentage composition*, $H = 4{\cdot}54$; $P = 46{\cdot}96$; $O = 48{\cdot}50$.

Properties.—A syrupy liquid, crystallisable below 0°, very soluble in water, easily oxidised to phosphoric acid. Like phosphorous acid, it is decomposed on heating into phosphoretted hydrogen and ordinary phosphoric acid—

$$2\,H_3PO_2 = PH_3 + H_3PO_4.$$

Like phosphorous acid, it is a reducing agent, but even more powerful, and precipitates metallic copper from solutions of its salts. It is a monobasic acid, containing 3 atoms of hydrogen in its molecule, but only one hydroxyl group.

Preparation.—By decomposition of its barium salt, $Ba(H_2PO_2)_2$,* with dilute sulphuric acid, and careful evaporation of the clear solution.

COMPOUNDS OF PHOSPHORUS AND HYDROGEN.

1. *Gaseous phosphoretted hydrogen*, $PH_3 = 34$.—This gas is inflammable, but not spontaneously inflammable, unless containing vapour of liquid phosphoretted hydrogen; it has a nauseous odour, resembling that of decaying fish. It has a strong analogy to ammonia in its properties.

2. *Liquid phosphoretted hydrogen*, $P_2H_4 = 66$.—This is a very volatile liquid, the vapour of which is spontaneously inflammable.

Preparations of Hydrogen Compounds of Phosphorus. — 1. *By heating phosphorus with a solution of a caustic alkali or alkaline earth.*—If phosphorus in small pieces is heated with a solution of potash, soda, lime, or baryta, gaseous and liquid phosphoretted hydrogen are evolved, and the mixed gases take fire on bubbling out of warm water into air. The reactions involved are represented by the following equations:—

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* See Preparation of phosphoretted hydrogen below.

$$\overset{\text{Potash.}}{3KHO} + \overset{\text{Phosphorus.}}{4P} + \overset{\text{Water.}}{3H_2O} = \overset{\text{Potassium Hypophosphite.}}{3KH_2PO_2} + \overset{\text{Gaseous Phosphoretted Hydrogen.}}{PH_3}.$$

$$\overset{\text{Potash.}}{4KHO} + \overset{\text{Phosphorus.}}{6P} + \overset{\text{Water.}}{4H_2O} = \overset{\text{Potassium Hypophosphite.}}{4KH_2PO_2} + \overset{\text{Liquid Phosphoretted Hydrogen.}}{P_2H_4}.$$

Potassium hypophosphite remains in the flask, which should be provided with a wide delivery tube to prevent fragments of phosphorus, liable to be thrown up by the bubbling liquid, from blocking the apparatus.

If the gaseous mixture is passed directly through a U-tube surrounded by a freezing mixture, the volatile liquid compound (P_2H_4) is condensed, and the gaseous compound (PH_3) passes on, and is found not to be spontaneously inflammable.

2. *By heating phosphorous acid, or hypophosphorous acid, or their salts*, phosphoretted hydrogen is given off, which is not spontaneously inflammable.

3. *By acting on calcium phosphide with water;* the gas obtained is spontaneously inflammable.

PHOSPHORUS TRICHLORIDE.

$PCl_3 = 137{\cdot}5$. Percentage composition, $P = 22{\cdot}5$, $Cl = 77{\cdot}5$. Liquid at ordinary temperatures. Specific gravity, 1·45 (water = 1). Boiling point, 78°.

Properties.—A colourless fuming liquid. In contact with water it forms phosphorous and hydrochloric acids, with evolution of much heat.

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

It unites readily with chlorine to form the pentachloride (PCl_5).

Preparation.—By passing chlorine over phosphorus heated nearly to boiling in a retort, the phosphorus being in excess.

PHOSPHORUS PENTACHLORIDE.

$PCl_5 = 208{\cdot}5$. Percentage composition, $P = 14{\cdot}86$, $Cl = 85{\cdot}14$. Solid at ordinary temperatures.

Properties.—A pale yellow crystalline, fuming, very volatile solid, which sublimes below 100° and melts under pressure at about 148°. Its vapour is very irritating.

Preparation.—By passing chlorine over phosphorus trichloride.

$$PCl_3 + Cl_2 = PCl_5.$$

PHOSPHORUS OXYCHLORIDE.

$POCl_3$ = 153·5. *Percentage composition*, *O* = 10·43; *P* = 20·19; *Cl* = 69·38. *Liquid at ordinary temperatures. Boils at* 110°. *Specific gravity*, 1·69 (*water* = 1).

Properties.—A colourless fuming liquid. In contact with water it forms phosphoric and hydrochloric acids.

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Preparation.—1. By exposing phosphorus pentachloride to moist air.

2. By distilling a mixture of phosphorus pentachloride and phosphoric anhydride.

$$3PCl_5 + P_2O_5 = 5POCl_3.$$

Other Compounds of Phosphorus.—Six sulphides of phosphorus are known, their formulæ being respectively P_4S, P_2S, P_4S_3, P_2S_3, P_2S_5, P_2S_{12}. Two bromides are known—PBr_3 and PBr_5, and two iodides—PI_3 and P_2I_4.

GENERAL CHARACTERISTICS OF THE NON-METALS.

Occurrence.—The majority of the most abundant and widely-diffused elements are found among the non-metals. Some, like oxygen, sulphur, carbon, nitrogen, and hydrogen, are found both in the free state and in combination, the rest occur in combination only, chiefly in the form of oxygen compounds or in direct combination with metals.

Physical Characters.—All physical conditions are represented among the non-metals. They include, on the one hand, the most solid, so to speak, of all elements—namely, carbon; and, on the other, the most persistently gaseous—namely, hydrogen. Four, or probably five, are gaseous at ordinary temperature and pressure—viz., oxygen, hydrogen, nitrogen, chlorine, and fluorine; one is fluid—viz., bromine, the rest are solid. They are all bad conductors of heat and electricity.

Chemical Character.—All non-metals, except fluorine, yield compounds with oxygen, most of them several, and all these are either neutral or acid-forming oxides, not one being basic. In this respect they have a number of analogues among the metals, such as arsenic and antimony. As regards special characters they fall into several well-marked families or groups.

Hydrogen and *boron*—stand, among the non-metals, by themselves, but both have several, more or less well marked, analogues among the metals. Hydrogen is uni-valent, boron tri-valent.

The group consisting of *fluorine*, *chlorine*, *bromine*, and *iodine* show striking similarities, more particularly the three last. They are all, in the main, uni-valent, although (particularly in the case of iodine) some of their compounds are best explained on the assumption of their being tri- or quinqui-valent. They are all characterised by great chemical activity, even at ordinary temperatures, and more especially by their strong affinity for hydrogen, with which element they each form one compound. Owing to this great affinity for hydrogen they are powerful oxidising agents in the presence of water. The affinity for hydrogen diminishes as we pass from fluorine to chlorine, bromine, iodine; the affinity for oxygen, on the other hand, increases. All except fluorine yield compounds with oxygen. Notwithstanding the difference in chemical character between these elements and hydrogen, they are capable of replacing hydrogen in many organic compounds without alteration of the typical character of the original compound. Such compounds are called substitution compounds (p. 78). No allotropic modifications of these elements are known. Their compounds with metals closely resemble the salts of the oxygen acids, and hence they are sometimes termed *halogens*, or salt formers.*

Another group—*oxygen*, *sulphur*, *selenium*, and *tellurium*—consist, like the preceding, of one member, oxygen, standing in some respects by itself, associated with a group of three most closely related elements. Oxygen is bi-valent, the others are bi-, quadri-, or sex-valent. They are comparatively inactive at ordinary temperatures, extremely active at elevated temperatures; their hydrogen compounds are closely analogous, and the three last form corresponding oxygen compounds. Proceeding from sulphur to tellurium the affinity for hydrogen increases, while that for oxygen diminishes. They yield allotropic modifications.

Another group consists of two members only—*carbon* and *silicon*. They are either bi-, but more generally quadri-valent, and are remarkable for the variety of strikingly different allotropic modifications which they yield. They are inactive at ordinary, very active at elevated, temperatures. Their affinity for hydrogen is feeble, but that for oxygen extremely powerful at high temperatures, on which account carbon is frequently employed as a reducing agent in metallurgy. Their most remarkable characteristic, however, is perhaps the power possessed by their atoms of combining with each other to form complex atoms or molecules, the valency of which is equal to twice the number of atoms combined, plus two. Carbon is *par excellence* the organic element, and no substance is called organic which does not contain it.

Finally the group—*nitrogen* and *phosphorus*—also consists, among non-metals, of two members only, but they have several well-marked analogues among the metals. They are mainly tri-valent, sometimes quinqui-valent. The chief characteristic of the one, viz., nitrogen, is great chemical inertness of the element, and the comparative instability of its compounds, nearly all of which have to be produced in an indirect manner, and the formation of which is frequently accompanied by absorption of heat. No allotropic modification of it is known. Nitrogen is pre-eminently characteristic of animal substances, and it is present more particularly in every animal structure or tissue. Phosphorus, on the other hand, possesses considerable chemical activity, and unites directly with many elements. Its combinations,

* ἅλς, *salt*, and γεννάω, *I produce.*

particularly those with oxygen, are accompanied with much evolution of heat. It forms two strikingly different allotropic modifications. Both elements form several compounds with hydrogen, of which, ammonia and phosphoretted hydrogen, possess, in presence of water, basic properties. This property is most marked in the case of ammonia, much less marked in the case of phosphoretted hydrogen, and almost disappears in the case of the corresponding hydrogen compounds of the metallic analogues. Both form several compounds with oxygen of corresponding composition.

Preparation.—Notwithstanding the fact that several of the non-metals are found in the free state in nature in very considerable quantities, all of them must be, as a rule, prepared from one or other of their compounds. The only practical exceptions to this are carbon in the forms of diamond and graphite (used only as found native), nitrogen and sulphur. The non-metals are prepared, nearly always, from their compounds with either hydrogen or oxygen by acting on these with elements having a stronger affinity for hydrogen or oxygen, as the case may be, than the non-metal to be prepared. Thus, chlorine, bromine, and iodine, for example, are prepared from their hydrogen compounds, by oxidising the hydrogen into water. Boron, silicon, and phosphorus, on the other hand, are prepared from their oxygen compounds by acting on these at elevated temperatures with an alkali metal, or with carbon, elements which, under these conditions, have greater affinity for oxygen than the above three non-metals.

THE METALS.

ALKALI METALS.[*]

POTASSIUM.
SODIUM.
LITHIUM.
CÆSIUM.
RUBIDIUM.
AMMONIUM.

POTASSIUM.

(*Potassa, Latinised form of pot-ash, hence potassium*[†]) $K = 39{\cdot}1$. *Specific gravity of solid*, 0·865 (*water* = 1), *of vapour*, 18·85 ($H=1$). *Melting point*, 62·5°. *Boiling point between* 719° *and* 731°. *Specific heat*, 0·166. *Monad.*

Occurrence in Nature.—Potassium never occurs in the free state, but in combination with sulphuric, nitric, hydrochloric, carbonic, phosphoric, silicic, and with various organic acids, is found very widely distributed in nature, in all kinds of natural waters, in all fruitful soils, in plants, and in the animal body. Among minerals in which it is an essential constituent may be mentioned *potash-felspar* or *orthoclase* ($K_2\,Al_2\,Si_6\,O_{16}$), *leucite* ($K_2\,Al_2\,Si_4\,O_{12}$), *sylvine* ($K\,Cl$), *carnallite* ($K\,Cl$, $Mg\,Cl_2$, $6\,H_2\,O$), and *kainite* ($Mg\,Cl_2$, $Mg\,S\,O_4$, $K_2\,S\,O_4$, $6\,H_2\,O$).

Properties.—Potassium is a bright, silver-white metal, lighter than water, and soft enough to be easily cut with a knife at ordinary temperatures, but is brittle at lower temperatures. It may be obtained in crystals belonging to the regular system. It melts at 62·5°, and volatilises at a red heat, yielding a green vapour, which imparts a bright violet colour to the flame, the spectrum of which is very characteristic (see plate). Both the violet colour and the spectrum are yielded by all volatile compounds of potassium.

Potassium is characterised by a strong attraction for oxygen. Owing to this attraction a bright surface of the metal can only be seen at the moment of cutting it with a knife, for a white film of oxide is immediately formed, and the oxidation rapidly proceeds throughout the mass if left exposed to the air for any length of time. If heated in

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[*] *Alkali*, from the Arabian *al-qaliy*, the "calcined ashes" of the plants *Salsola* and *Salicornia*, from *qalay*, to roast or fry in a pan, hence transferred to the plants themselves so used. In early chemistry *alkali* was supposed to be a specific substance which existed *fixed* in potash and soda, *volatile* in ammonia. Duhamel, in 1736, showed that there were three distinct alkalies, and these were distinguished as *mineral alkali* (soda), *vegetable alkali* (potash), and *animal alkali* (ammonia). The word alkali is now applied more especially to the hydrates of the above metals, but in a more general sense to the hydrates of barium, strontium, and calcium, hence the term *alkaline earths* (p. 225), and to the *alkaloids* or organic ammonias (p. 112), hence also the term *alkaline reaction* applied to the behaviour of soluble bases to litmus, &c.—See further, Murray, *New English Dictionary*, 1885, *Part i.*, p. 223.

[†] Skeat.

contact with air it takes fire. It is a powerful reducing agent, and is often used as such in the laboratory.

It will decompose water at ordinary temperatures (see p. 105), forming potassium hydrate (KHO), and ejecting hydrogen, which, owing to the high temperature of the reaction, takes fire, and burns with a violet flame caused by a partial volatilisation of the metal.

For these reasons it has to be kept out of contact with oxygen, whether free or in combination, and is usually stored in naphtha or in hermetically sealed tubes. It combines readily also with sulphur, phosphorus, and chlorine (in which it burns with intense brilliancy), and forms a compound with hydrogen of a somewhat unstable nature.

At a red heat it deoxidises carbonic anhydride, separating out carbon, thus:—

$$\overset{\substack{\text{Carbonic}\\\text{Anhydride.}}}{CO_2} + \overset{\text{Potassium.}}{2K_2} = \overset{\substack{\text{Potassium}\\\text{Oxide.}}}{2K_2O} + \overset{\text{Carbon.}}{C.}$$

But at a white heat carbon deoxidises potassium oxide, forming carbonic oxide and potassium—

$$\overset{\text{Potassium Oxide.}}{K_2O} + \overset{\text{Carbon.}}{C} = \overset{\text{Carbonic Oxide.}}{CO} + \overset{\text{Potassium.}}{K_2.}$$

Manufacture and Preparation—1. *By the reduction of potassium carbonate with charcoal.*—Crude *tartar*, or acid tartrate of potassium ($KHC_4H_4O_6$), is first heated to a bright redness in a covered crucible, whereby an intimate mixture of charcoal and potassium carbonate is obtained. This mixture is then transferred to an iron retort, which is gradually heated to a bright red, or even white heat, in a furnace, and is connected with a flat-shaped iron receiver, in order that the potassium vapour may cool as quickly as possible. Great caution is necessary to avoid explosion from mechanical obstruction of the neck of the retort, or from the formation of an explosive compound of the potassium with carbonic oxide.

The reaction may be expressed as follows:—

$$\overset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} + \overset{\text{Charcoal.}}{C_2} = \overset{\text{Potassium.}}{K_2} + \overset{\substack{\text{Carbonic}\\\text{Oxide.}}}{3CO.}$$

2. By the electrolysis of fused potash. 3. By the action of iron filings on potassium sulphide at a red heat.

OXIDES OF POTASSIUM.

Potassium Monoxide, $K_2O = 94{\cdot}2$.—A white powder formed by oxidising potassium in dry air, free from carbonic anhydride. It is very deliquescent, and unites with great energy with water to form potassium hydrate.

Potassium Hydrate (*potash*, *caustic potash*, *potassa*, *potassium hydroxide*, &c.). $KHO = 56$. $[K_2O \,.\, H_2O]$. *Specific gravity*, 2·1 (*water* = 1).

Properties.—A white, crystalline, very deliquescent solid. It is extremely soluble in water (requiring less than its own weight of water for solution) and in alcohol; the solutions have a very alkaline reaction (restoring the blue colour to reddened litmus, turning turmeric paper brown, &c.), a soapy feeling and a nauseous taste. It acts as a powerful caustic on the skin. It possesses the characters of a basic oxide in a marked degree; thus, it absorbs carbonic anhydride from the air, forming potassium carbonate; it gradually dissolves silica from glass vessels, forming potassium silicate; and it neutralises all acids with formation of water and the corresponding potassium salts, *e.g.*:—

Potassium Hydrate.		Nitric Acid.		Potassium Nitrate.		Water.
KHO	+	HNO_3	=	KNO_3	+	H_2O.

It precipitates all metals which form insoluble hydrates from solutions of their salts as such hydrates, *e.g.* :—

Ferric Chloride.		Potassic Hydrate.		Ferric Hydrate.		Potassium Chloride.
Fe_2Cl_6	+	$6KHO$	=	$Fe_2O_3, 3H_2O$	+	$6KCl$.

It forms several crystalline hydrates with water. It melts at a dull red heat, and volatilises at a white heat without decomposition. It is much used in the laboratory as a reagent.

Physiological Action.—The solution when undiluted is a violent caustic poison. The solid is used externally as a caustic.

Manufacture and Preparation.—1. *From potassium carbonate by the action of lime.*—A ten per cent. solution* of potassium carbonate is first boiled in an iron vessel, and milk of lime (p. 233) gradually added in considerable excess, and the whole maintained at a boiling temperature for a short time. The mixture is then left to settle, and after subsidence of the solid matter (calcium carbonate and excess of lime), the clear liquor is drawn off, evaporated in an iron vessel till all the water is expelled, when the mass solidifies on cooling. Run into moulds in the form of thin bars, it forms the *stick potash* of commerce. The reaction which occurs may be represented as follows:—

Potassium Carbonate.		Lime.		Potassic Hydrate.		Calcium Carbonate.
K_2CO_3	+	CaH_2O_2	=	$2KHO$	+	$CaCO_3$.

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* If a more concentrated solution is used the action is reversed:—$2KHO + CaCO_3 = K_2CO_3 + CaH_2O_2$.

If required very pure, silver vessels may be substituted for iron ones, and the potash may be afterwards extracted with alcohol, by which means most of the impurities, including potassium carbonate, remain behind, being insoluble; the alcohol is removed by distillation.

2. *By heating a mixture of potassium nitrate and copper foil to redness* in a copper crucible and extracting the fused mass with water.

Other Oxides of Potassium.—Oxides of the formula $K_2 O_2$ and $K_2 O_4$ are also known, and are formed, by passing dry air or oxygen over the gently heated monoxide. When these oxides are acted on by water, they are decomposed with formation of hydrate of potassium and free oxygen. Ordinary stick potash, when dissolved in water, nearly always evolves some oxygen, producing a slight effervescence, owing to its containing some of these higher oxides.

SALTS OF POTASSIUM.

Neutral Potassium Carbonate (*normal potassium carbonate, pearl-ash, &c.*), $K_2 C O_3 = 138{\cdot}2$. *Specific gravity*, 2·2 (*water* = 1). *Melting point*, 838°.

Properties.—This salt is colourless, and crystallises with three molecules of water ($K_2 C O_3$, $3 H_2 O$). It is very deliquescent, and is soluble in less than its own weight of water; the solution has an alkaline reaction. It is insoluble in alcohol. On heating, it loses its water, and fuses at a red heat without change in composition.

Manufacture.—Potassium, as already stated, is found in land plants, and the greater part is usually present in them in combination with organic acids. When wood is incinerated these organic salts are decomposed with formation of potassium carbonate, which may be separated from the numerous other salts by extraction (lixiviation) with water. By evaporation of this solution *crude potash* is obtained. This is once more extracted with water, and the solution on evaporation yields the *pearl-ash* of commerce, containing about 80 per cent. of potassium carbonate.

A similar product is obtained from beet-root, from sea-weed, and from washings of sheep's-wool. Potassium carbonate is now also largely manufactured from potassium sulphate by a process distinctly analogous to the Leblanc process (*q.v.*, p. 213).

Preparation—1. *From pearl-ash.*—If pearl-ash is extracted with an equal weight of cold water, the hydrate, $K_2 C O_3$, $2 H_2 O$, crystallises out on concentrating the solution by evaporation.

2. *From acid tartrate of potassium* (*cream of tartar*, $K H C_4 H_4 O_6$)

—If this salt is heated to redness in a platinum crucible, it is converted into the carbonate, which may be purified by extracting with water and evaporating the solution to crystallisation. A very pure form of the salt is thus obtained.

Acid Potassium Carbonate (*bicarbonate of potash, hydric potassic carbonate, &c.*) $KHCO_3 = 100{\cdot}1$.

Properties.—This salt crystallises in large (monoclinic) crystals, which are not deliquescent. It is much less soluble than the neutral carbonate, requiring four times its weight of water for solution; 100 parts of water dissolve at 10°, 19·6 parts, at 20°, 23·2 parts. The solution is feebly alkaline, and gives off carbonic anhydride on boiling. The salt is decomposed at a moderate heat into normal carbonate, water, and carbonic anhydride.

$$\underset{\text{Acid Potassium Carbonate.}}{2KHCO_3} = \underset{\text{Normal Potassium Carbonate.}}{K_2CO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic Anhydride.}}{CO_2}.$$

Physiological Action.—It is largely used as an ant-acid.

Preparation.—By passing carbonic anhydride into a cold solution of potash—the salt, not being very soluble, separates out in crystals during the process, which may afterwards be purified by solution and recrystallisation.

Potassium Nitrate (*nitre, saltpetre*), $KNO_3 = 101{\cdot}1$. $[NO_2 . OK]$. *Specific gravity*, 2·1 (*water* = 1). *Melting point*, 339°.

Properties.—This salt is dimorphous. It usually crystallises in rhombic prisms, but may be obtained in rhombohedral crystals. It is not deliquescent. It is not very soluble in cold water, but its solubility increases very rapidly as the temperature rises. Thus, at 10° it requires five times its weight, but at 100° it is soluble in less than half its weight of water. Its solution is attended with considerable absorption of heat. Heated above 350°, it loses an atom of oxygen, forming potassium nitrite (KNO_2), and at a still higher temperature is completely decomposed into potassium oxide, nitrogen, and oxygen.

Owing to the facility with which it parts with its oxygen, it is a powerful oxidising agent; heated on charcoal it gives rise to a brisk combustion termed *deflagration;* sulphur, phosphorus, and many metals are oxidised when heated with it, with considerable rise of temperature.

Manufacture—1. *From natural saltpetre* (see nitric acid, p. 118)—by lixiviation of the earth or rock in which it occurs, and evaporation of the solution to crystallisation.

2. *From Chili saltpetre* ($NaNO_3$).—By mixing hot solutions of Chili saltpetre and potassium chloride, double decomposition ensues, the potassium nitrate being more soluble in the hot remains in solution, and the chloride of sodium crystallises out and is removed. The potassium nitrate solution is then run into crystallising pans and allowed to cool, and the nitre so obtained purified by recrystallisation.

3. *By the atmospheric oxidation of animal refuse in the presence of a strong base, and of a special kind of baccillus.*—This process, which is less used than formerly, is in imitation of the natural conditions under which saltpetre is formed. Animal matter is built up into heaps with carbonate of lime, and left exposed to the action of the atmosphere (but protected from rain), and watered from time to time with stale urine and with water. In the course of two or three years the nitrogenous matter is completely converted into nitrate of potassium or calcium, and the mass is lixiviated with water. The nitrate of calcium is converted into potassium nitrate by addition of potassium carbonate, by which means the calcium is precipitated as carbonate. The crude nitre so obtained undergoes further purification.

Preparation.—By neutralising nitric acid with potassium carbonate or with potash. By careful recrystallisation of the natural salt.

Gunpowder.—The composition of gunpowder has remained unaltered for many years, viz., saltpetre 75 parts, charcoal 15, sulphur 10. The charcoal employed is usually made from alder, willow, or black dogwood.

The materials are intimately mixed, in a moist state, in special *incorporating mills*, and finally *grained*, after which the powder is dried at a temperature of from 120° to 130° F. (48·9° to 54·5° C.)

The object of graining gunpowder, is to permit the flame to penetrate between the interstices of the grains, so as to allow of simultaneous combustion or explosion; if the interstices between the grains are filled with incombustible materials (such as glass or sand), so as to isolate the grains, the powder is no longer explosive. If the intimately mixed ingredients are reduced to a fine powder, the mixture only burns with greater or less rapidity, but produces no explosion unless confined.

Gunpowder explodes at a temperature of about 600° F, (315·5° C.) The chief effect of gunpowder is due to the combustion of the charcoal by the oxygen of the nitre; the sulphur is added to increase the inflammability of the mixture. The gaseous products evolved during the explosion of gunpowder (about 43 per cent. by weight of the powder used) are chiefly carbonic anhydride, carbonic oxide, and nitrogen; the solid products (about 57 per cent. of the powder used) consist for the most part of carbonate, sulphate, and sulphide of potassium.

One cubic inch of powder yields about 280 cubic inches of gas measured at 0° and 760 mm. Bar., but owing to the high temperature at the moment of explosion (about 4000° F. or 2200° C.) the pressure exerted is equal to about 6400 atmospheres, or some 42 tons to the square inch, if the powder is exploded in a space which it entirely fills; if the powder does not entirely fill the space, or if such space be enlarged in consequence of the explosion, the pressure becomes less in proportion.

The total amount of work done by the explosion of 1 lb. of gunpowder is equal to 480 *foot-tons;* that is, by means of the explosion of 1 lb. of gunpowder we could raise 480 tons 1 foot high, or 1 ton 480 feet high.

Normal or Neutral Potassium Sulphate, $K_2SO_4 = 174{\cdot}2$. $[SO_2(OK)_2; K_2O, SO_3]$. *Specific gravity*, 2·66 (*water* = 1). *Melting point, above* 861°.

Properties.—This salt crystallises in transparent, anhydrous, rhombic prisms. It is soluble in 8 parts of cold water and in 4 parts of boiling, but is insoluble in alcohol. On heating it decrepitates, and at a red heat melts without change of composition.

Preparation.—By neutralising sulphuric acid with potassic carbonate or hydrate.

Manufacture.—Obtained as a bye-product in various manufacturing processes, as, for example, from the mother-liquors in the preparation of carbonate of potassium from wood-ashes, of soda from kelp, from sea-water, &c.

Acid Potassium Sulphate (*hydrogen potassium sulphate, bisulphate of potash*), $KHSO_4 = 136{\cdot}1$. $[SO_2 . OH . OK]$. *Specific gravity*, 2·16. (*water* = 1). *Melting point*, 210°.

Properties.—This salt crystallises in rhombic prisms. It is much more soluble than the neutral sulphate, requiring twice its weight of water at 15·5°, and less than its own weight at 100°. The solution has a sour taste and acid reaction. It melts at 210°, and at about 600° it is decomposed into neutral sulphate, sulphuric acid, sulphurous acid, and oxygen.

Preparation.—By evaporating to dryness neutral sulphate of potassium with half its weight of strong sulphuric acid.

Potassium Monosulphide, $K_2S = 110{\cdot}2$.

Properties.—This salt crystallises in colourless crystals. It is very deliquescent and very soluble in water. Its solution dissolves the sulphides of arsenic, antimony, and tin.

Preparation.—1. By heating to redness a mixture of potassium sulphate and charcoal:—$K_2SO_4 + 4C = K_2S + 4CO$. 2. Or, in aqueous solution, by dividing a solution of potassium hydrate into two equal parts and mixing after saturating one-half with sulphuretted hydrogen.

Hydric Potassic Sulphide (*potassium sulphydrate*). $KHS = 72{\cdot}1$.

This salt is the analogue of potassic hydrate (KHO), which it resembles in many respects. It can be obtained in very deliquescent crystals.

Preparation.—By saturating a solution of potassium hydrate with sulphuretted hydrogen:—$KHO + H_2S = KHS + H_2O$.

Polysulphides of Potassium, K_2S_2, K_2S_3, K_2S_4, K_2S_5.—These are prepared by fusing the monosulphide (or heating its solution) with sulphur

Hepar Sulphuris (*liver of sulphur, potassa sulphurata*).

This is a pharmaceutical preparation, made by heating potassium carbonate and sulphur in a crucible, and consists of pentasulphide and thiosulphate or sulphate of potassium, according to the temperature at which it is prepared.

Potassium Chlorate, $KClO_3 = 122{\cdot}6$. $[ClO_2 . OK]$. *Specific gravity*, 2·32 (*water* = 1). *Melting point*, 359°.

Properties.—This salt crystallises in tabular crystals. It is not very soluble in water, requiring sixteen times its own weight at ordinary temperatures, but only twice its weight of boiling water for solution. It melts at 359°, and at a somewhat higher temperature begins to decompose. Heated on charcoal it deflagrates.

Combustible substances, mixed with chlorate of potassium, yield explosive mixtures, many of which are readily exploded by percussion. During the combustion of such mixtures, more heat is evolved than by the burning of the combustible substance in oxygen; the heat reaction in the formation of the chlorate being negative (Chap. xii.)

Preparation.—By passing chlorine into a solution of potassium carbonate mixed with a sufficient amount of milk of lime to contain 5 molecules of hydrate of calcium to 1 molecule of potassium carbonate, and separating the difficultly soluble potassium chlorate from the readily soluble calcium chloride by crystallisation.

$$\overset{\text{Potassium Carbonate.}}{K_2CO_3} + \overset{\text{Lime.}}{5CaH_2O_2} + \overset{\text{Chlorine.}}{6Cl_2} = \overset{\text{Potassium Chlorate.}}{2KClO_3} + \overset{\text{Calcium Chloride.}}{5CaCl_2} + \overset{\text{Water.}}{5H_2O} + \overset{\text{Carbonic Anhydride.}}{CO_2}.$$

Potassium Perchlorate, $KClO_4 = 138{\cdot}6$. $[ClO_3 . OK]$. *Specific gravity*, 2·52 (*water* = 1). *Melting point*, 610°.

This salt crystallises in rhombic octahedra. It is very difficultly soluble in water (1 in 60). Like the chlorate it is decomposed by heat.

Preparation.—By heating potassium chlorate until it has lost about 9 per cent. of oxygen, and separating the perchlorate so formed by crystallisation.

$$\overset{\text{Potassium Chlorate.}}{2KClO_3} = \overset{\text{Potassium Perchlorate.}}{KClO_4} + \overset{\text{Potassium Chloride.}}{KCl} + \overset{\text{Oxygen.}}{O_2}.$$

It is also produced when the chlorate is acted on by strong sulphuric acid.

Potassium Chloride, $KCl = 74{\cdot}6$. *Specific gravity*, 1·9 (*water* = 1). *Melting point*, 734°.

Occurrence.—Found dissolved in sea water, in many mineral waters, and either pure (*sylvine*) or combined with chloride of magnesium (*carnallite*) in various rock salt deposits. It is the predominant alkaline chloride in the juice of flesh.

Properties.—This salt crystallises in cubes. It is soluble in three times its weight of water at ordinary temperatures with great depression of temperature, and in twice its weight at 100°. It is insoluble in alcohol. It combines with platinic chloride ($Pt\,Cl_4$) to form a difficultly soluble double salt ($K_2\,Pt\,Cl_6$).

Preparation.—From the mother-liquor of evaporated sea water; but chiefly by the recrystallising of carnallite.

Potassium Bromide, $KBr = 119{\cdot}1$. *Specific gravity,* 2·69 (*water* = 1). *Melting point,* 699°.

Properties.—This salt crystallises in cubes. It is soluble in twice its weight of water at ordinary temperatures, and in about its own weight at 100°. It is also soluble in alcohol.

Physiological Action (see p. 181).

Preparation.—1. By neutralising hydrobromic acid with potassium hydrate or carbonate. 2. By acting on a solution of potassium hydrate with bromine, evaporating to dryness, heating the resulting mixture of bromide and bromate with charcoal, and recrystallising.

Potassium Iodide, $KI = 166{\cdot}1$. *Specific gravity,* 3·0 (*water* = 1). *Melting point,* 634°.

Properties.—This salt crystallises in cubes. Both the salt and its solution become slightly yellow on exposure to air, owing to slight decomposition by carbonic anhydride. It is soluble in rather less than its own weight of water at ordinary temperatures. Its saturated solution boils at 120°, and contains 68·9 per cent. of the salt. It is soluble in alcohol. Its aqueous solution dissolves iodine. When free from iodate, the solution remains colourless on addition of hydrochloric acid.

Physiological Action (see p. 184).

Preparation.—By methods strictly analogous to the preparations of the bromide. By acting with iodine on iron in the presence of water and decomposing the resulting iodide of iron by potassium carbonate, $Fe + I_2 = Fe\,I_2$; $Fe\,I_2 + K_2\,C\,O_3 = Fe\,C\,O_3 + 2\,K\,I$.

Distinguishing Tests of the Potassium Salts.—Not too dilute solutions of the potassium salts yield, with *platinum tetrachloride,* a yellow crystalline precipitate ($2\,K\,Cl, Pt\,Cl_4$), insoluble in alcohol, soluble in a solution of potassium hydrate; with a concentrated solution of *tartaric acid* or *acid sodium tartrate,* a white crystalline precipitate ($K\,H\,C_4\,H_4\,O_6$), insoluble in alcohol, soluble in solutions of potassium hydrate or hydrochloric acid; with a solution of *hydrofluosilicic acid,* a gelatinous precipitate ($K_2\,Si\,F_6$), insoluble in alcohol. Potassium salts give a *violet-coloured flame* when introduced on a platinum wire into the flame of a Bunsen burner; this flame yields a characteristic spectrum and appears purple-red through an indigo prism or cobalt-blue glass.

Potassium salts are all white, unless the acid is coloured; nearly all soluble in water, easily fusible, and volatile only at a high temperature.

SODIUM.*

Na = 23. *Specific gravity of solid*, 0·972 (*water* = 1), *of vapour*, 12·75 (*H* = 1). *Melting point*, 97·6°. *Boiling point*, *between* 861° *and* 954°. *Specific heat*, 0·293. *Monad.*

Occurrence in Nature.—The most common compound of this metal, which only occurs in combination, is its chloride, generally known as *salt* (rock salt, common salt); this substance is found in immense deposits in various parts of the world, in sea water and in mineral waters, and is always present, though in small quantities, in ordinary drinking water. It is even found in air, and is, in fact, so widely diffused, that its presence may always be demonstrated by its very delicate spectroscopic reaction. As nitrate it also occurs in considerable deposits. It further occurs largely as carbonate, sulphate, and phosphate, &c., and is a constituent of numerous silicates, among which may be mentioned *sodalite* ($2\,NaCl$, $3\,Na_2\,Al_2\,Si_2\,O_8$) and *albite* ($Na_2\,Al_2\,Si_6\,O_{16}$). It is found in the ash of all plants, more particularly of sea plants, in which it is the predominating alkali metal, and in most parts of the animal body, especially the blood, the aqueous humour of the eye, urine, &c.

Properties.—Sodium is a bright, silvery-white metal resembling potassium very closely in its physical properties, but not quite so soft. Both the metal and its compounds impart an intense yellow colour to the flame, the spectrum of which is also highly characteristic. Like potassium, it may be distilled. It crystallises in the regular system.

Sodium further resembles potassium in its chemical properties very closely—thus, it has a very strong attraction for oxygen, and, as in the case of potassium, the bright surface of the metal can only be perceived at the moment of cutting it, owing to the rapid oxidation which takes place on its surface. Heated in contact

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* Old Italian, *soda*, an ash from which glass is made. Old French, *soulde*, glasswort, answers to Latin *solida*, *hard*.—Skeat.

with air it takes fire, burning with an intense yellow flame. Like potassium, it is also a powerful reducing agent, and is often used as such in the laboratory. It decomposes water at ordinary temperatures (see Hydrogen, p. 100), forming sodium hydrate ($Na\,H\,O$), and liberating hydrogen, which, however, is not ignited unless the water is warm or present only in small quantity (if, for example, a piece of sodium is thrown on to wet blotting-paper, the hydrogen which is evolved ignites and burns with an intense yellow flame). It resembles potassium in all other respects and, like that metal, has to be preserved under naphtha (*cf.* potassium, p. 203).

Preparation.—By decomposing fused caustic soda with a mixture of spongy iron and carbon:—$6\,Na\,H\,O + Fe + C_2 = 2\,Na_2\,C\,O_3 + 3\,H_2 + Fe + Na_2$ (Kastner).

OXIDES OF SODIUM.

Two oxides of sodium are known, viz., *sodium monoxide*, $Na_2\,O$, and *sodium dioxide*, $Na_2\,O_2$; they are analogous in their properties to the corresponding oxides of potassium.

Sodium Hydrate (*sodium hydroxide, soda, caustic soda*), $Na\,H\,O = 40$. [$Na_2\,O, H_2\,O$]. *Specific gravity*, 2·1 (*water* = 1).

Properties.—This compound is in every respect analogous in its properties to the corresponding potassium hydrate ($K\,H\,O$). It is very deliquescent, and, also, like potassium hydrate, it absorbs carbonic anhydride, becoming coated with sodium carbonate, which is, however, not (like potassium carbonate) deliquescent; so that when sodium hydrate is exposed to the air it becomes at first moist, but, finally, dries up again. It is volatile at a white heat. It is soluble in 2½ parts of water at ordinary temperature. The solution has a specific gravity of 1·5 and is strongly caustic, but less so than the solution of potassium hydrate.

Physiological Action.—Analogous to that of potassium hydrate but less powerful.

Preparation.—1. *From sodium carbonate by the action of lime* (*cf.* potassium hydrate, p. 204). 2. *Very pure* by the action of sodium on water and evaporation of the solution in silver vessels.

SALTS OF SODIUM.

Neutral Sodium Carbonate (*technically known as soda*), $Na_2\,CO_3$, $10\,H_2\,O = 106 + 180 = 286$. *Specific gravity*, 1·45 (*water* = 1). *Melting point*, 34°; *of anhydrous*, 814°.

Occurrence in Nature.—Sodium carbonate is found as an effloresence on the soil in many parts of Hungary, and dissolved in the water of various lakes in Hungary, Egypt, Persia, India, and China, and in Russian and Turkish Armenia.

Properties.—This salt crystallises in well formed, colourless, transparent crystals, belonging to the monoclinic system, and containing 62·9 per cent. water of crystallisation. It is extremely efflorescent, becoming white and opaque on exposure to air; it loses one-half its water at 12·5°.

It is extremely soluble in water. The solubility increases up to 38°, but begins to decrease at higher temperatures (100 parts water dissolve 12·06 parts of the anhydrous salt at 10°, 51·67 at 38°, and 45·47 at 104°).* The solution is alkaline and caustic. On heating, the salt melts in its water of crystallisation, which at a higher temperature is completely driven off leaving anhydrous sodium carbonate, Na_2CO_3, which melts at a red heat without undergoing further change. The anhydrous salt has a specific gravity of 2·46. It forms various other hydrates, containing one, seven, nine, and fifteen molecules of water.

Manufacture—From sodium chloride.—Sodium carbonate is obtained from common salt by processes which are carried out on an enormous scale, and form a highly important branch of chemical industry.

Leblanc Process.—This process, named after its inventor, was discovered in 1793, and consists mainly in the conversion of common salt into sodium sulphate, the reduction of this salt to sulphide by means of coal, and, finally, the conversion of the sulphide into carbonate by treatment with calcium carbonate.

The sodium chloride is converted into sulphate by treatment with sulphuric acid in a suitable furnace; immense quantities of hydrochloric acid gas are given off, which is absorbed in water; the acid sulphate is first formed, and finally the neutral sulphate :—

Sodium Chloride.		Sulphuric Acid.		Sodium Sulphate.		Hydrochloric Acid.
$2NaCl$	$+$	H_2SO_4	$=$	Na_2SO_4	$+$	$2HCl$.

This is called the *salt-cake* process. The crude anhydrous sodium sulphate (*salt-cake*) is next intimately mixed with small coal and chalk or limestone, and heated to redness in a special reverberatory furnace; the reaction which ensues may be expressed by the following equations :—

Sodium Sulphate.		Carbon.		Sodium Sulphide.		Carbonic Oxide.
Na_2SO_4	$+$	$4C$	$=$	Na_2S	$+$	$4CO$.

* The ordinary crystals dissolve in two parts of cold and in less than their own weight of boiling water.

$$\overset{\text{Sodium Sulphide.}}{Na_2S} + \overset{\text{Calcium Carbonate.}}{CaCO_3} = \overset{\text{Sodium Carbonate.}}{Na_2CO_3} + \overset{\text{Calcium Sulphide.}}{CaS.}$$

The black mass which results (*soda ash, black ash, ball soda*), is extracted with water, whereupon impure sodium carbonate dissolves and the calcium monosulphide remains behind. The impure sodium carbonate, obtained from this solution by evaporation, which still contains sulphate, sulphide, and various other impurities, is once more heated with coal, and is finally purified by crystallisation.

The residual calcium monosulphide, known as *alkali waste*, contains all the sulphur from the sulphuric acid used. It was formerly thrown away, but now generally undergoes special treatment for the recovery of its sulphur.

2. *The Ammonia-soda Process.*—This process is based on the double decomposition which ensues when a solution of ammonium bicarbonate (NH_4HCO_3) is brought into contact with a solution of sodium chloride, resulting in the precipitation of the somewhat difficultly soluble sodium bicarbonate, while the ammonium chloride simultaneously formed goes into solution.

In actual practice carbonic anhydride and ammonia gases are passed into a solution of common salt. The reaction may be expressed as follows:—

$$\overset{\text{Sodium Chloride.}}{NaCl} + \overset{\text{Ammonia.}}{NH_3} + \overset{\text{Water.}}{H_2O} + \overset{\text{Carbonic Anhydride.}}{CO_2} = \overset{\text{Sodium Bicarbonate.}}{NaHCO_3} + \overset{\text{Ammonium Chloride.}}{NH_4Cl.}$$

The ammonium chloride by treatment with lime (p. 129) yields up its ammonia, which can thus be used over and over again.

Simple as the process appears, it is nevertheless beset with many practical difficulties, but is now successfully worked on a very large scale.

3. *Cryolite Process.*—This depends on the decomposition of cryolite ($3\,NaF, AlF_3$) when heated with calcium carbonate, with formation of soluble sodium aluminate and insoluble calcium fluoride:—

$$\overset{\text{Cryolite.}}{2[(NaF)_3AlF_3]} + \overset{\text{Limestone.}}{6\,CaCO_3} = \overset{\text{Sodium Aluminate.}}{Al_2O_3\,3\,Na_2O}$$

$$+ \overset{\text{Calcium Fluoride.}}{6\,CaF_2} + \overset{\text{Carbonic Anhydride.}}{6\,CO_2.}$$

The sodium aluminate is dissolved out and carbonic anhydride passed through the solution — alumina is precipitated and sodium carbonate goes into solution.

$$Al_2 O_3 3 Na_2 O + 3 C O_2 = 3 Na_2 C O_3 + Al_2 O_3.$$

4. Sodium carbonate was formerly manufactured from the ash of plants growing on the sea-shore (species of *salsola* and *salicornia*) and from the ash of sea-weed (called *kelp*), which is now only used as a source of iodine (*q.v.*)

Acid Sodium Carbonate (*sodium bicarbonate*), $Na H C O_3 = 84$.

Properties.—This salt crystallises in monoclinic crystals. It is difficultly soluble in water, requiring about ten times its weight at ordinary temperatures. 100 parts of water dissolve 10·04 parts of the salt at 10°, and 16·69 parts at 70°. Its solution is slightly alkaline. On heating the salt or its solution, it is more or less rapidly converted into the neutral carbonate. It is used very extensively in the preparation of effervescing powders.

Physiological Action.—Analogous to that of the corresponding potassium salt (p. 206).

Preparation.—It is prepared, like the analogous potassium salt (*q.v.*, p. 206), by mixing 1 part of crystallised soda with 3 parts of anhydrous soda, and exposing the mixture to the action of carbonic anhydride.

Sodium Sesquicarbonate, $Na_4 H_2 (C O_3)_3, 2 H_2 O = 274 + 36 = 310$. $[2 Na_2 C O_3, H_2 C O_3; Na_2 C O_3, 2 Na H C O_3]$.

Occurrence in Nature.—This salt is found dissolved in the waters of some inland seas in Africa and North America, and as an incrustation on the shores or deposited on the bottom of these lakes. It is known as *Trona* in Africa, and as *Urao* in America.

Properties.—It crystallises in prisms, belonging to the monoclinic system, which do not effloresce in air. 100 parts of water dissolve 18·3 parts of the salt at 20°, 55·8 parts at 80°, and 41·6 parts at 100°.

Preparation.—It may be obtained by cooling a concentrated solution of bicarbonate which has been boiled for some time, or by precipitating with alcohol a solution of 10 parts neutral carbonate and 15 parts of bicarbonate in 190 parts of water.

Sodium Nitrate (*chili saltpetre, cubic nitre*), $Na N O_3 = 85$. $[N O_2 . O Na]$. *Specific gravity*, 2·1 (*water* = 1). *Melting point*, 316°.

Occurrence in Nature.—It is found in considerable deposits in Peru and Chili, mainly on the elevated plateaux (3000 feet), where little or no rain falls.

Properties.—This salt resembles potassium nitrate closely, but, unlike that salt, is rather deliquescent, and cannot, therefore, be used in the manufacture of gunpowder. It crystallises in rhombohedra, the shape of the crystals closely approaching that of a cube, whence its name of *cubic nitre.* It is dimorphous, and may be obtained in prismatic crystals, like those of ordinary nitre. It is much more soluble than ordinary nitre.

Uses.—It is used as a manure, and in the manufacture of nitric acid, and in the manufacture of potassium nitrate by double decomposition with potassium chloride.

Manufacture.—From the natural product by recrystallisation.

Neutral Sodium Sulphate (*Glauber's salt*), $Na_2\,S\,O_4,\ 10\,H_2\,O = 142 + 180 = 322$. $[S\,O_2\,(O\,Na)_2]$. *Specific gravity*, 1·46 (*water* = 1). *Melting point*, 34°; *of anhydrous*, 861°.

Occurrence in Nature.—In the lakes in which carbonate of soda is found (p. 212), in many mineral waters—*e.g.*, Carlsbad; in sea water; in considerable deposits in Spain, sometimes anhydrous (*Thénardite*), sometimes in the form of double salts with sulphate of calcium (*Glauberite*), or sulphate of magnesium (*Blödite*), sometimes as the hydrated salt.

Properties.—This salt crystallises in large colourless, efflorescent, monoclinic crystals containing 55·76 per cent. of water of crystallisation. It is very soluble in water, requiring about twice its weight at ordinary temperatures; up to 34° its solubility increases, but beyond that temperature it diminishes—thus, 100 parts of water dissolve 9 parts of the anhydrous salt at 10°, 55 parts at 34°, and 42·5 parts at 100°. When heated it loses its water of crystallisation, becoming anhydrous. It forms other hydrates, and may be also obtained in anhydrous crystals from solution.

Physiological Action.—Purgative.

Preparation.—The anhydrous salt is obtained as a bye product in the manufacture of nitric acid (p. 118), and is also formed during the manufacture of sodium carbonate. It may be prepared by neutralising sulphuric acid with sodium carbonate.

Acid Sodium Sulphate (*hydric sodic sulphate*, *bisulphate of soda*), $Na\,H\,S\,O_4 = 120$. $[S\,O_2\,.\,O\,H\,.\,O\,Na]$.

Properties.—This salt crystallises in triclinic crystals. It is very soluble in water. The solution has an acid reaction. When carefully heated, the salt loses water, forming the pyrosulphate, $Na_2\,S_2\,O_7$, and on further heating is converted into the neutral sulphate, with evolution of sulphuric anhydride.

Preparation.—By evaporating the neutral sulphate to dryness with sulphuric acid.

Sodium Thiosulphate (*sodium hyposulphite*), $Na_2 S_2 O_3, 5 H_2 O = 158 + 90 = 248$. $[S O_2 . O Na . S Na.]$ *Specific gravity*, 1·7 (*water* = 1). *Melting point*, 45°.

Properties.—This salt crystallises in colourless crystals, belonging to the monoclinic system, which are permanent in dry air, and very readily soluble in water. The crystals, melt in their own water of crystallisation at a temperature of 45°, and this liquid on cooling readily yields a supersaturated solution, which solidifies rapidly with considerable evolution of heat on introduction of even a minute piece of the solid salt. Heated to 100° the crystals lose their water, and on stronger heating sulphur is separated, and a mixture of sulphate and sulphide of sodium is left behind.

The salt is used largely as an antichlore—*i.e.*, for preventing the injurious effects of chlorine left in goods bleached by the same. Its solution has remarkable solvent powers, and, among other salts, readily dissolves the halogen compounds of silver, on which account it is largely used in photography. In solution it is converted by iodine into tetrathionate of soda and iodide of sodium ($2 \mathrm{Na_2 S_2 O_3} + \mathrm{I_2} = \mathrm{Na_2 S_4 O_6} + 2 \mathrm{Na I}$), which reaction is made use of for the volumetric estimation of iodine, as well as of substances which liberate iodine.

Manufacture.—By boiling a solution of sodium sulphite with sulphur, and crystallising.

Sodium Chloride (*salt, common salt*), $Na Cl = 58·5$. *Specific gravity.* 2·15 (*water* = 1). *Melting point*, 772°.

Occurrence in Nature (see sodium, p. 211).—It is the predominating alkaline chloride in the blood and urine.

Properties.—This salt crystallises in regular cubes. It is not deliquescent.[*] It requires about two-and-a-half times its weight of water at ordinary temperatures for solution, and its solubility does not increase to any extent with the temperature; 100 parts by weight of water dissolve 35·87 parts of the salt at 14°, and 39·61 parts at 100°.

It decrepitates on heating, melts at a red heat, and is volatile at high temperatures. Under certain conditions (for example, from solutions containing a certain quantity of urea) it crystallises in octahedra.

Manufacture.—The manufacture of common salt consists practically in (1) the purification by solution and crystallisation of the naturally

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[*] Unless contaminated with magnesium chloride.

occurring rock salt, (2) in the concentration and ultimate crystallisation of the salt occurring in natural brine springs, and (3) in the evaporation of sea-water. In (2) and (3) the greater portion of the evaporation is effected by means of solar heat.

Disodic Hydric Phosphate (*phosphate of soda*), $Na_2HPO_4, 12H_2O =$ $142 + 216 = 358$. $[PO.OH.(ONa)_2]$. *Specific gravity*, 1·52 (*water* = 1). *Melting point*, 35°.

Properties.—This is the most commonly known of the various sodium phosphates. It crystallises in monoclinic prisms, and contains 60·3 per cent. of water of crystallisation. It is efflorescent. It is extremely soluble in hot water, but less so in cold. 100 parts by weight of water dissolve 3·9 parts of the anhydrous salt at 10°, 24·1 parts at 30°, and 98·8 at 99°. The saturated solution boils at 105°.

On heating, the salt first melts in its water of crystallisation, and loses it entirely at a comparatively gentle heat. At a higher temperature two molecules of the anhydrous salt lose one molecule of water, becoming converted into pyrophosphate—

$$\overset{\text{Disodic Hydric Phosphate.}}{2Na_2HPO_4} - \overset{\text{Water.}}{H_2O} = \overset{\text{Sodium Pyrophosphate.}}{Na_4P_2O_7}.$$

A solution of the salt has a slightly alkaline reaction; it gives a yellow precipitate with nitrate of silver (triargentic phosphate), and the solution becomes acid, thus:—

$$\overset{\text{Disodic Hydric Phosphate.}}{Na_2HPO_4} + \overset{\text{Argentic Nitrate.}}{3AgNO_3} = \overset{\text{Triargentic Phosphate.}}{Ag_3PO_4} + \overset{\text{Sodic Nitrate.}}{2NaNO_3} + \overset{\text{Nitric Acid.}}{HNO_3}.$$

Preparation.—By neutralising a solution of tribasic phosphoric acid with carbonate of sodium, and crystallising.

Sodium Biborate (*borax*), $Na_2B_4O_7$, $10H_2O = 202 + 180 = 382$. $[2NaBO_2, B_2O_3]$. *Specific gravity*, 1·7 (*water* = 1). *Melting point*, 75·5°; *of anhydrous*, 561°.

Occurrence in Nature (see p. 148).

Properties.—This salt crystallises in colourless rhombic prisms, which are permanent in air. When heated they melt in their water of crystallisation, swell up considerably, becoming anhydrous, and finally melt to a clear transparent glass. 100 parts of water dissolve only 2·53 parts at 0°, but 40·43 parts at 60°, and 201·43 parts at 100°.

Melted borax is a solvent for many metallic oxides, and is on that account largely used in the soldering and melting of metals. It is also used as a flux in metallurgical operations, and as a blowpipe reagent in the laboratory (see *boric acid*, p. 149).

Manufacture.—1. By adding boric acid to a boiling solution of carbonate of soda, and crystallising (to 1,200 parts of crystallised soda about 1,000 parts of commercial boric acid). 2. By the recrystallisation of native borax (p. 148).

Distinguishing Tests of Sodium Salts.—Sodium salts yield no precipitate with any of the ordinary reagents; they impart an intense yellow colour to the flame of a Bunsen burner when introduced into it on the loop of a platinum wire. The colour of the flame is almost monochromatic, and when examined with a spectroscope of sufficient dispersive power yields two bright lines absolutely coincident with the D lines of the solar spectrum. The reaction is of exceeding delicacy (see p. 44). The sodium salts are all white, unless the acid is coloured; they are soluble in water, with, perhaps, the sole exception of the metantimonate ($Na_2 Sb_2 O_7$); they are easily fusible; and volatile at high temperatures.

LITHIUM.

(λίθος, *a stone*[*]). *Li* = 7; *Li*$_2$ = 14. *Specific gravity*, 0·59 (*water* = 1). *Specific heat*, 0·9408.
Melting point, 180°. *Monad.*

Occurrence in Nature.—Lithium occurs in certain minerals, such as *triphyllin*, a phosphate of iron, manganese, &c., and in certain aluminic silicates, such as *petalite*, *spodumene*, *lepidolite*, &c., of which it constitutes from 1 to 5 per cent. It also occurs in certain mineral springs, notably at Wheal Clifford in Cornwall, and is widely diffused in the vegetable and animal kingdoms. It is, however, one of the rarer elements.

Properties.—A soft, white metal, closely resembling potassium and sodium in its properties. It is the lighest solid known. It is not so soft nor so oxidisable as potassium or sodium. It can be welded; and pressed into wire. Thrown upon water, it decomposes it without melting and without ignition of the hydrogen evolved. It forms an oxide ($Li_2 O$) and a hydrate ($Li H O$), in all respects analogous to the corresponding potassium and sodium compounds.

Lithium Salts.—Lithium forms a series of salts analogous to the potassium and sodium salts. The carbonate ($Li C O_3$) is difficultly soluble in water, and the phosphate ($Li_3 P O_4$) practically insoluble; so that in concentrated solutions of lithium salts ammonium carbonate produces a precipitate, and from dilute solutions the phosphate is precipitated by a soluble phosphate.

Lithium salts impart a brilliant red colour to the flame of a Bunsen burner; the lithium spectrum is characterised by an intense red line, and a much feebler orange line, and constitutes after sodium the most delicate of spectrum reactions.

Preparation.—By electrolysis of the fused chloride ($Li Cl$).

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[*] In reference to the supposition that lithium occurred only in the mineral kingdom; since shown to be erroneous.

CÆSIUM.

[*Cæsius, blue*[*] *(of the sky)*]. *Cs* = 133. *Specific gravity*, 1·88 (*water* = 1). *Melting point*, 27°. *Monad.*

Occurrence in Nature.—Occurs closely associated with rubidium in minute quantities in certain mineral springs, notably in that of Dürkheim and Wheal Clifford; and in certain minerals, especially a rare silicate *Pollux* occurring in the Isle of Elba, which contains 34 per cent. of the oxide.

Properties.—Like rubidium, it is almost indistinguishable in its properties from potassium, except in its spectrum, which is characterised by two bright blue lines almost coinciding with the strontium blue line, Sr δ. The metal, obtained by electrolysis of the chloride, takes fire in air. It is the most electro-positive of all the metals.

A number of its salts are known; the carbonate is soluble in absolute alcohol, while rubidium carbonate is nearly insoluble; the tartrate is also much more soluble than the corresponding rubidium tartrate. With platinum chloride, solutions of cæsium salts yield a precipitate much less soluble than the corresponding potassium compound. The separation of potassium, cæsium, and rubidium, is based on these facts.

Preparation.—By electrolysis of the chloride.

RUBIDIUM.

(*Rubidus, dark red*[†]). *Rb* = 85·2. *Specific gravity*, 1·5 (*water* = 1). *Melting point*, 38°.

Occurrence in Nature.—Rubidium occurs, usually accompanied by cæsium, in minute quantities, and very widely diffused in many mineral waters and minerals.

Properties.—Like cæsium, it is only readily distinguishable from potassium by its spectrum, which contains two violet lines lying between the blue strontium line, Sr δ, and the blue potassium line, κ β, and two red lines beyond Fraunhofer's line A in the outermost portion of the red end of the spectrum.

It is less rapidly oxidisable than cæsium; it decomposes water when thrown on it, and the hydrogen evolved is ignited. It is more electro-positive than potassium. It forms a number of salts; it may be separated from potassium and cæsium in the manner described under cæsium.

Preparation.—The metal may be prepared in an analogous manner to potassium from the tartrate.

AMMONIUM ($Am' = NH_4 = 18$).

It has already been shown (p. 128) that when ammonia enters into combination with an acid, it does not, like the metals, replace the hydrogen of the acid, but combines with the whole molecule forming salts analogous to those of potassium and sodium. It has been consequently assumed that there exists in these salts a compound radical of the formula, NH_4, which plays the part of a metal, and to it has been given the name *ammonium*.

An apparent confirmation of this theory is afforded by the fact that, when sodium amalgam[‡] is brought into contact with a solution of

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[*] In reference to the bright blue lines of its spectrum.

[†] In reference to the dark red lines in its spectrum.

[‡] A compound of mercury and sodium.

ammonium chloride, the mercury swells up into a peculiar buttery mass lighter than water, but of metallic appearance, like mercury, and containing from 0·6 to 0·9 per cent. of ammonium. This compound (?), to which the name *ammonium amalgam* has been given, breaks up rapidly at ordinary temperatures into mercury, hydrogen, and ammonia. Its bulk varies under variations of pressure somewhat like a gas, and it is, therefore, held by many to be mercury distended with these gases. It may be noted, however, that neither ammonia nor hydrogen are soluble in mercury under ordinary conditions.

Ammonium Hydrate, $NH_4HO = 35$. $[NH_3, H_2O; AmHO]$.

A solution of ammonia in water may, in accordance with the above theory, be regarded as the hydrate of the hypothetical metal ammonium, and the analogue of the hydrates of the alkali metals.

SALTS OF AMMONIUM.

Neutral Ammonium Carbonate $(NH_4)_2CO_3, H_2O = 96 + 18 = 114$. $[Am_2CO_3]$.

Properties.—This salt is very unstable, and decomposes spontaneously on exposure to air, giving off ammonia, and becoming converted into the acid carbonate, NH_4HCO_3.

Preparation.—It is prepared, with some difficulty, by digesting commercial carbonate of ammonia with a strong solution of ammonia, when it separates out as a crystalline powder.

Acid Ammonium Carbonate (*ammonium bicarbonate*), $NH_4HCO_3 = 78$. $[AmHCO_3]$. *Specific gravity*, 1·58 (*water* = 1).

Occurrence in Nature.—This salt is found in Patagonian guano.

Properties. — It may be obtained in large rhombic crystals, soluble in about eight times their weight of water. The solution undergoes decomposition even at ordinary temperatures, rapidly at higher temperatures, ammonia being evolved.

Preparation.—By saturating a solution of ammonia or of the sesquicarbonate with carbonic anhydride, or by digesting the sesquicarbonate with strong alcohol, which dissolves out all but the bicarbonate.

Ammonium Sesquicarbonate (*tetrammomio-dihydric carbonate, half-acid carbonate*), $N_4H_{18}C_3O_9 = 254$. $[(NH_4)_2CO_3, 2NH_4HCO_3; Am_2CO_3, 2AmHCO_3; Am_4H_2(CO_3)_3]$.

Properties.—This salt is a double salt containing two molecules of ammonium bicarbonate, combined with one molecule of neutral carbonate, and is decomposed by treatment with water or alcohol into these two salts.

It may be obtained in rectangular prisms, which rapidly decompose in air, with formation of the bicarbonate and evolution of ammonia.

Physiological Action.—Similar to that of ammonia (p. 128).

Preparation.—By digesting the commercial carbonate with ammonia at about 30°.

Commercial Carbonate of Ammonia (*sal volatile*, *salt of hartshorn*), $N_3\,H_8\,C_2\,O_5 = 150$. $[N\,H_4\,H\,C\,O_3,\ N\,H_4\,C\,O_2\,N\,H_2]$.

Properties.—This salt is a mixture of bicarbonate ($\mathrm{Am\,H\,C\,O_3}$) and *carbamate of ammonium* ($\mathrm{N\,H_4\,C\,O_2\,N\,H_2}$). It is a white fibrous mass, possessing a strong smell of ammonia, which it is constantly evolving.

Manufacture.—1. By the dry distillation of bones, hartshorn, and other animal matter, and re-sublimation. 2. By heating to redness a mixture of chalk ($\mathrm{Ca\,C\,O_3}$) and sal ammoniac ($\mathrm{Am\,Cl}$) or ammonium sulphate ($\mathrm{Am_2\,S\,O_4}$).

Ammonium Nitrate, $N\,H_4\,N\,O_3 = 80$. $[Am\,N\,O_3;\ N\,O_2 . O\,Am]$. *Specific gravity*, 1·7 (*water* = 1).

Properties.—This salt crystallises in six-sided prisms belonging to the rhombic system. It is deliquescent. It is soluble in half its weight of cold water, with great depression of temperature.

On gently heating it first melts and then splits up into water and nitrous oxide (*q.v.*, p. 120), but at higher temperatures into nitrogen, nitric oxide, and water.

Preparation.—By neutralising nitric acid with ammonium carbonate. If the salt is to be employed in the preparation of laughing-gas (p. 120) care should be taken that the nitric acid and ammonium carbonate are free from chlorine compounds.

Ammonium Sulphate $(N\,H_4)_2\,S\,O_4 = 132$. $[Am_2\,S\,O_4;\ S\,O_2\,(O\,Am)_2]$. *Specific gravity*, 1·75 (*water* = 1).

Properties.—This salt crystallises in six-sided rhombic prisms. It is soluble in twice its weight of cold and in an equal weight of hot water. On heating it melts at 140°, but above 180° is completely decomposed.

Preparation.—The salt is manufactured in a manner distinctly analogous to the preparation of chloride of ammonium from the ammonia water of gas-works, &c. (see p. 134), or by neutralising dilute sulphuric acid with ammonium carbonate.

Ammonium Monosulphide (*ammonium sulphide*), $(N\,H_4)_2\,S = 68$. $[Am_2\,S]$.

This salt may, with difficulty, be obtained in crystals which are extremely soluble in water, and which, when exposed to the air, give off ammonia, and are converted into ammonium hydrosulphide (see below).

The aqueous solution is much used as a reagent in the laboratory. It is at first colourless, but becomes yellow on exposure to air, and finally colourless again, with considerable deposition of sulphur.

Preparation.—The aqueous solution is obtained by saturating one-half of a solution of ammonia with sulphuretted hydrogen (whereby ammonium hydrosulphide is formed), and adding the product to the other half.

Ammonium Hydrosulphide, $NH_4HS = 51$. $[AmHS]$.

Properties.—This salt may be obtained in colourless needles at 0°, which sublime at ordinary temperatures. Its solution is much used as a reagent in the laboratory; it becomes yellow on standing.

Preparation.—Its aqueous solution is obtained by saturating a solution of ammonia with sulphuretted hydrogen.

Ammonium Chloride (*sal ammoniac*), $NH_4Cl = 53{\cdot}5$. $[AmCl]$. *Specific gravity*, 1·5 (*water* = 1).

Occurrence.—Found in the neighbourhood of volcanoes.

Properties.—This salt may be obtained in cubes and in octahedra, but, when sublimed, is fibrous in structure. It is soluble in less than 3 parts of cold water with great depression of temperature; 100 parts of water dissolve 28·4 parts of the salt at 0°, 32·8 parts at 10°, and 77·2 parts at 100°. The saturated solution boils at 115°. On heating at a moderate temperature it sublimes without decomposition, but at higher temperatures it undergoes dissociation (see p. 76). It forms double salts with the chlorides of magnesium, nickel, cobalt, manganese, zinc, and copper, from solutions of which the hydrated oxides of these metals can no longer be precipitated by solutions of the hydroxides of the alkali metals. It is used for the preparation of ammonia in the laboratory.

Manufacture and Preparation.—It was formerly extracted from camels' dung by sublimation. It is largely manufactured from the ammonia water of gas-works (p. 134) by neutralisation with hydrochloric acid and subsequent purifications, and similarly from the ammonia compounds obtained in the dry distillation of bones. It may be prepared pure by subliming the commercial salt.

Physiological Action.—It is largely used in medicine—its action is not well understood, but appears to be stimulant.

Hydrogen Di-Ammonium Phosphate (*ammonium phosphate*) $(NH_4)_2$, $HPO_4 = 132$. $[Am_2HPO_4;\ PO\,.\,OH\,.\,(OAm)_2]$. *Specific gravity*, 1·64 (*water* = 1).

Occurrence in Nature.—It is found in guano.

Properties.—This salt closely resembles the corresponding phosphates of sodium and potassium. It crystallises in monoclinic crystals which are easily soluble in water. It is the most easily obtained and most stable of the ammonium phosphates, and is much used as a reagent in the laboratory.

Preparation.—By saturating a solution of phosphoric acid with ammonium carbonate and evaporating with constant addition of ammonia.

Sodium Ammonium Phosphate (*microcosmic*[*] *salt*), NH_4NaHPO_4, $4H_2O = 137 + 72 = 209$. [$PO.OH.ONa.OAm$]. *Specific gravity*, 1·6 (*water* = 1).

Properties.—This salt crystallises in monoclinic, slightly efflorescent crystals, which are easily soluble in water; the solution has an alkaline reaction.

On heating, it loses its water of crystallisation and, at a red heat, is converted into sodium metaphosphate with evolution of ammonia.

$$NH_4NaHPO_4 = NaPO_3 + NH_3 + H_2O.$$

It is used in the laboratory for the same purpose as borax (p. 218), since the sodium metaphosphate ultimately formed on fusing it possesses, like borax, the property of dissolving metallic oxides, forming a characteristically-coloured, glass-like bead.

Preparation.—By mixing solutions of ammonium chloride and di-sodium hydrogen phosphate and evaporating to crystallisation.

$$Na_2HPO_4 + AmCl = AmNaHPO_4 + NaCl.$$

The sodium chloride formed remains in the mother-liquor. The salt may be purified by recrystallisation.

Distinguishing Characters of the Ammonium Salts.—Concentrated solutions of ammonium salts yield, with a concentrated solution of *platinum tetra-chloride*, a yellow precipitate ($2AmCl, PtCl_4$), and, with a strong solution of tartaric acid, or with *acid sodium tartrate*, a white crystalline precipitate ($AmHC_4H_4O_6$), neither of which are distinguishable to the eye from the corresponding potassium compounds (p. 210), but which may be easily shown to contain ammonia.

Boiled with *potassium or sodium hydrate*, or with lime, ammonium salts yield ammonia gas, which may be recognised by its smell, &c. (*cf.* p. 128).

A solution of mercuric iodide in potassium iodide solution, made strongly alkaline with potassium hydrate (*Nessler's test*), yields a brown

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[*] *Sal microcosmicum* (μικρός, *little*, and κόσμος, *a world*), so called from its occurrence in the human body.

coloration with a minute trace of an ammonium salt in solution; with stronger solutions it yields a brown precipitate.

Ammonium salts are white, unless the acid is coloured. On heating they are all decomposed, and *completely volatilised*, unless the acid they contain is fixed, in which case ammonia only is driven off. When pure, ammonium salts impart no colour to the flame of a Bunsen burner.

METALS OF THE ALKALINE EARTHS.

BARIUM. | STRONTIUM. | CALCIUM. | (MAGNESIUM.)

BARIUM.

(*βαρύς, heavy*). *Ba*=137. *Specific gravity*, 3·6 (*water*=1).
Fuses at a red heat. Dyad.

Occurrence in Nature.—Barium occurs chiefly as sulphate (*barytes*, or *heavy spar*, $Ba\,S\,O_4$), and as carbonate (*witherite*, $Ba\,C\,O_3$). It occurs in far smaller quantities in certain silicates and other minerals, in sea water, and in some mineral waters—but always in combination.

Properties.—The properties of this metal, owing to the difficulty of its preparation, have not been much studied. It is a yellowish or silver-white metal, malleable, and melts only at red heat. It gradually oxidises in contact with air. It decomposes water at ordinary temperatures. Heated in air, it takes fire and burns with a greenish flame, forming barium oxide.

Preparation.—The metal was first obtained by the electrolysis of baryta in the presence of mercury, and the amalgam formed was heated, with exclusion of air to drive off the mercury. Bunsen recommends the electrolysis of a paste of barium chloride and dilute hydrochloric acid at 100° in the presence of mercury, and heating the crystalline amalgam so formed in a current of hydrogen, whereupon the barium is left as a porous mass.

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* In allusion to the high specific gravity of its sulphate, known as *barytes* or *heavy spar*.

OXIDES OF BARIUM.

Barium Monoxide (*baryta*), $Ba\ O = 153$.

Properties.—A gray, amorphous powder, which combines with water, with great evolution of heat, forming barium hydrate. It is fusible at a high temperature.

Preparation.—By heating barium nitrate to redness.

Barium Hydrate (*barium hydroxide, baryta hydrate*), $Ba\ H_2\ O_2 = 171$. [$Ba\ (H\ O)_2$; $Ba\ O,\ H_2\ O$]. *Specific gravity*, 4·495 (*water* = 1).

Properties.—This substance crystallises in prisms or tables containing eight molecules (45·7 per cent.) of water of crystallisation ($Ba\ H_2\ O_2, 8\ H_2\ O$). At a gentle heat seven molecules of water are expelled, the eighth is driven off at a red heat; the residual hydrate ($Ba\ H_2\ O_2$) fuses without change of composition, and solidifies on cooling to a crystalline mass. It is far more soluble in hot than in cold water, requiring about twenty times its weight of cold, but only twice its weight of boiling water for solution. The solution (*baryta water*) is very alkaline, and rapidly becomes turbid on exposure to air owing to its attraction for carbonic anhydride, and the consequent formation of the insoluble barium carbonate ($Ba\ C\ O_3$). It is a valuable reagent in the laboratory, and is much used for the absorption and estimation of carbonic anhydride.

Preparation.—1. by decomposing a hot concentrated solution of barium chloride with a solution of caustic soda, and allowing crystallisation to take place out of contact with air.

2. By boiling a solution of barium sulphide with cupric oxide—

$$Ba\,S + Cu\,O + H_2\,O = Ba\,H_2\,O_2 + Cu\,S.$$

Barium Dioxide (*peroxide of barium*), $Ba\ O_2 = 169$.

Properties.—A gray or, when pure, a white powder which, at a bright red heat, yields up part of its oxygen forming the monoxide—$Ba\ O_2 = Ba\ O + O$.

In contact with cold water it forms a crystalline hydrate containing 6 molecules of water; the same hydrate is formed by adding peroxide of hydrogen to baryta water. When acted upon by sulphuric or hydrochloric acid it yields the corresponding barium salt and peroxide of hydrogen (*q.v.*, p. 111) which goes into solution.

Preparation.—By heating barium monoxide in a current of air or oxygen to a temperature between 300° and 400°. 2. By heating barium monoxide with potassium chlorate to redness in a platinum crucible, and extracting the fused mass with cold water, whereupon the potassium chloride dissolves out, leaving the peroxide behind.

SALTS OF BARIUM.

Barium Carbonate, $Ba\,C\,O_3 = 197$. *Specific gravity*, 4·3 (*water* = 1).

Occurrence in Nature.—The mineral called *witherite* consists of barium carbonate.

Properties.—Artificially prepared it is a white powder which is very sparingly soluble in water. (It is, however, more soluble than barium sulphate, and requires 14,000 times its weight of water for solution at ordinary temperatures. It is still less soluble in water at higher temperatures.) It is much more soluble in water containing carbonic anhydride in solution, probably owing to the formation of an acid carbonate. At 10°, 1 part of carbonate dissolves in 588 parts of water saturated with carbonic anhydride. The acid carbonate readily breaks up into neutral carbonate and carbonic anhydride.

It is much used in the preparation of barium salts. On strongly heating it loses carbonic anhydride.

Preparation.—By precipitating a solution of barium chloride with a solution of a carbonate of one of the alkali metals.

Barium Nitrate, $Ba\,(N\,O_3)_2 = 261$. $[(N\,O_2)_2 \,.\, O_2\,Ba]$. *Specific gravity*, 3·2 (*water* = 1). *Melting point*, 593°.

Properties.—This salt crystallises in transparent colourless octahedra; 100 parts of water dissolve 7 parts of the salt at 10°, and 32·2 parts at 100°. It is difficultly soluble in the presence of free nitric acid.

Use.—It is employed for the production of various kinds of explosives containing nitro-cellulose.

Preparation.—By dissolving the carbonate in nitric acid, filtering the solution and evaporating to crystallisation.

Barium Sulphate, $Ba\,S\,O_4 = 233$. $[S\,O_2 \,.\, O_2\,Ba]$. *Specific gravity*, 4·4 (*water* = 1).

Occurrence in Nature.—This salt occurs in nature, and is known as *heavy spar* or *barytes*. It is often found in crystals belonging to the rhombic system, which have a specific gravity of 4·48.

Properties.—Artificially prepared it is a white, very fine powder. It is practically insoluble in water, requiring 400,000 times its weight for solution. With sulphuric acid, in which it is to a certain extent soluble, it forms a crystalline compound.

It is insoluble in hydrochloric or nitric acid, and is converted with difficulty into carbonate by boiling with a solution of excess of a carbonate of an alkali (*cf.* strontium sulphate). The pulverised mineral is used as a paint.

Preparation.—By precipitation from a solution of barium chloride, by sulphuric acid, or a soluble sulphate.

Barium Sulphide, $Ba\,S = 169$.

Properties.—This salt, which is not easily obtained pure, is chiefly of interest on account of its preparation from the sulphate, and from the fact that it is largely used for the preparation of other barium salts. It is a white powder, soluble in water, and may be obtained in colourless crystals, containing 6 molecules of water of crystallisation ($Ba\,S, 6\,H_2\,O$).

Preparation.—Finely powdered barium sulphate is mixed with one-fourth of its weight of powdered charcoal and enough oil to make the mixture into a stiff paste. This mixture is maintained at a bright red heat for some time, the mass is extracted with boiling water when, on cooling, barium sulphide crystallises out.

Barium Chloride, $Ba\,Cl_2, 2\,H_2\,O = 208 + 36 = 244$. *Specific gravity,* 3·1 (*water* = 1). *Melting point of anhydrous, above* 860°.

This salt crystallises in tabular crystals belonging to the rhombic system. It contains two molecules of water which are easily expelled by heat; 100 parts of water dissolve 42·5 parts of the salt at 15·5°. The saturated solution boils at 104·5, and contains 78 per cent. of the salt.

Preparation.—1. By dissolving the carbonate or sulphide in hydrochloric acid, filtering the solution and evaporating to crystallisation. 2. By strongly heating a mixture of sulphate of barium with half its weight of chloride of calcium and rapidly extracting the heated mass with water.

Barium Chlorate, $Ba\,Cl\,O_3, H_2\,O = 220{\cdot}5 + 18 = 238{\cdot}5$. *Specific gravity,* 3·0 (*water* = 1). *Melting point of anhydrous,* 414°.

Properties.—Crystallises in colourless prisms belonging to the monoclinic system. Soluble in 4 parts of cold water, scarcely soluble in alcohol. Heated to 120° it loses its molecule of water, and at higher temperatures breaks up into chloride and oxygen. With combustible substances it yields mixtures which explode by percussion or heat, or burn with a brilliant green light. It is used in pyrotechny for the production of green fires and stars.

Preparation.—By neutralising a solution of chloric acid with barium carbonate, and evaporating to crystallisation. It is produced, together with barium chloride, by passing chlorine into a hot solution of barium hydrate, but cannot well be separated from the chloride (*cf.* potassium chlorate, p. 209).

Distinguishing Characters of Barium Salts.—All the soluble salts of barium and the carbonate are poisonous. They are all white, unless the acid is coloured. They vary considerably in fusibility, some being practically infusible. Of the more common salts the sulphate, carbonate, and phosphate are insoluble in water.

Solutions of barium salts yield with a solution of *ammonium carbonate* (or any carbonate of the alkalies) a white precipitate ($Ba\,C\,O_3$) soluble with effervescence in dilute acids; with *sulphuric acid* or a soluble sulphate an immediate white precipitate insoluble in hydrochloric acid, even on boiling; with *hydrofluosilicic acid* a transparent precipitate in not too dilute solutions; with *potassium chromate* a yellow precipitate insoluble in acetic acid.

Barium salts (especially if moistened with strong hydrochloric acid), when introduced on a loop of platinum wire into a Bunsen or blowpipe flame, impart to it a vivid pale green coloration, the spectrum of which is characterised by a series of bright bands in the green.

STRONTIUM.*

Sr = 87·5. *Specific gravity*, 2·5 (*water* = 1). *Melts at a red heat. Dyad.*

Occurrence in Nature.—Strontium belongs to the rarer class of elements. It is chiefly found as sulphate (*celestine*, $Sr\,S\,O_4$), and as carbonate (*strontianite*, $Sr\,C\,O_3$). It is found also accompanying barium and calcium in some minerals, and is present in minute quantities in most natural waters.

Properties.—Strontium is a yellowish metal, harder than lead or calcium, malleable, and melts at a gentle red heat. It oxidises easily, and burns to oxide when heated in air, and with a brilliant crimson flame. It decomposes water energetically at ordinary temperatures.

Preparation.—By the electrolysis of the fused chloride, with special precautions to prevent the oxidation of the metal.

Oxides of Strontium.—Strontium forms a monoxide ($Sr\,O$), also called strontia and its hydrate ($Sr\,H_2\,O_2$), and a dioxide ($Sr\,O_2$) and its hydrate ($Sr\,O_2$, $8\,H_2\,O$), all of which are analogous in their properties to the corresponding barium compounds; but the hydrate loses its water at a red heat, and the dioxide cannot be prepared by heating the monoxide in a current of air, but must be precipitated as the hydrate from a solution of the hydroxide by addition of a solution of peroxide of hydrogen, and this, on careful drying, yields the anhydrous dioxide.

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* *Strontianite* ($Sr\,C\,O_3$) was first found in and named after the village of Strontian in Argyllshire; hence the name of the metal.

SALTS OF STRONTIUM.

Strontium Carbonate, $Sr\,C\,O_3 = 147{\cdot}5$. *Specific gravity*, 3·6 (*water* = 1).

Occurrence in Nature.—This salt is found in nature in the mineral *strontianite.* It is found in crystals isomorphous with *arragonite* ($Ca\,CO_3$).

Properties.—When artificially prepared, it is a white powder. It is very sparingly soluble in water, requiring 18,000 times its weight of water for solution. When heated to a red heat, it yields up carbonic anhydride.

Preparation.—By precipitating a solution of strontium nitrate with a solution of a carbonate of an alkali.

Strontium Nitrate, $Sr\,(N\,O_3)_2 = 211{\cdot}5$. $[(N\,O_2)_2 \,.\, O_2\,Sr]$. *Specific gravity*, 2·8 (*water* = 1). *Melting point*, 645°.

This salt crystallises in anhydrous octahedra, but may also be obtained in monoclinic crystals of the formula, $Sr\,(N\,O_3)_2, 4\,H_2\,O$. It is very deliquescent. 100 parts of water dissolve 40·16 parts of the salt at 10°, and 101·1 parts at 100°. It is insoluble in nitric acid. The salt has been used in pyrotechny, on account of the brilliant crimson colour which it imparts to a flame, but owing to its deliquescent character it is a dangerous constituent in firework compositions; a mixture of strontium carbonate and potassium chloride is now generally substituted for it.

Preparation.—By solution of the carbonate of strontium in nitric acid.

Strontium Sulphate, $Sr\,S\,O_4 = 183{\cdot}5$. $[S\,O_2 \,.\, O_2\,Sr]$. *Specific gravity*, 3·9 (*water* = 1).

Occurrence in Nature.—This salt is found in nature in the mineral *celestine*, crystallised in the rhombic system.

Properties.—This salt may be obtained crystalline from its solution in strong sulphuric acid, with which it also forms a crystalline compound. It is very difficultly soluble in water; 100 parts of water dissolve 0·0145 parts of the salt at ordinary temperatures, and 0·0104 at 100°. It is more easily soluble in water containing certain salts in solution. On boiling with a solution of a carbonate of an alkali, it is converted into strontium carbonate (*cf.* barium sulphate, p. 227).

Preparation.—By precipitation of a solution of strontium nitrate with sulphuric acid, or a solution of a soluble sulphate.

Distinguishing Characters of the Salts of Strontium.—Strontium salts are white, unless the acid they contain is coloured; in regard to their solubility they closely resemble barium salts. Solutions of the salts yield, with *alkaline or ammonium carbonates*, a white precipitate soluble with effervescence in hydrochloric acid. When not too diluted they yield, with *soluble sulphates*, a white precipitate of sulphate of strontium, the production of which is greatly facilitated by boiling. Placed in the flame of a Bunsen burner on a loop of a platinum wire, particularly in the form of chloride, they impart to the flame an intense crimson colour, which, when examined by the spectroscope, shows a number of brilliant, orange and red lines, together with one very brilliant line in the blue.

They can best be distinguished from calcium salts by the spectrum reaction, or by the fact that their solution, when not too dilute, yields a precipitate after a time, or quickly on heating, on addition of a solution of calcium sulphate, but not with a solution of strontium sulphate.

CALCIUM.

(*Calx, lime*), *Ca* = 40. *Specific gravity*, 1·57 (*water* = 1). *Specific heat*, 0·167. *Melts at a red heat. Dyad.*

Occurrence in Nature.—Calcium is one of the most abundant and widely diffused of the elements, but it occurs always in combination and chiefly as *carbonate;* in this form it constitutes some of the most common minerals and rocks—*e.g.*, *arragonite*, *calc-spar*, *chalk*, *limestone*, *marble;* it is a constituent of *dolomite* ($Ca\,C\,O_3$, $Mg\,C\,O_3$); it occurs as *sulphate* in anhydrite ($Ca\,S\,O_4$), and in *gypsum* or *alabaster* and in *selenite* ($Ca\,S\,O_4$, $2\,H_2\,O$); as *fluoride* in *fluor-spar* ($Ca\,F_2$); as *phosphate* in *apatite* [$Ca\,F_2$, $3\,Ca_3\,(P\,O_4)_2$]; as *silicate* it is very widely diffused in numerous minerals. Many of its salts are normal constituents of soils, of plants, and of the animal body; egg-shells, coral, and the shells of mollusca consist chiefly of calcium carbonate, bones consist chiefly of calcium phosphate. The carbonate (held in solution by free carbonic anhydride) and sulphate are also normal constituents of natural waters, and are contained in sea water.

Properties.—The metal calcium is somewhat yellow, harder than lead, ductile and malleable. It oxidises slowly in dry air, more rapidly in the presence of moisture; it must be preserved out of contact with air. Heated in air to a bright red heat it melts and ignites, burning with a bright white light, and forming calcium oxide. It decomposes water at ordinary temperatures.

Preparation.—1. By the electrolysis of a fused mixture of calcium chloride, strontium chloride, and a little ammonium chloride (Matthiessen). 2. By reducing calcium chloride with metallic sodium;

by heating to redness a mixture of calcium chloride, granulated zinc, and sodium, an alloy of zinc and calcium is obtained, which on further heating in a crucible of gas carbon, yields a button of calcium, the zinc volatilising (Caron).

OXIDES OF CALCIUM.

Calcium Monoxide (*lime,* quicklime*), $Ca\,O = 56$. *Specific gravity,* 3·08 (*water* = 1).

Properties.—A white amorphous solid (generally very porous, owing to its method of preparation), which attracts water and carbonic anhydride from the air, and combines with great energy and with much evolution of heat with water to form calcium hydroxide ($Ca\,O + H_2\,O = Ca\,H_2\,O_2$).

When water is poured upon quicklime the latter swells up, cracks, emits steam, and finally falls to an impalpable dry powder. The purer the lime the more rapidly do these phenomena ensue; a lump of commercial quicklime may be held in the hand and rapidly dipped into water three or four times; each time a hissing sound is heard, but the lump remains dry when taken out, and, if then placed on a plate, in a few minutes goes through all the phenomena above described.

Calcium monoxide is infusible even in the oxyhydrogen blowpipe; when so heated it becomes white hot, and emits an intensely brilliant light; use is made of this fact in the well-known lime-light of Drummond.

Preparation.—1. Pure oxide of calcium is best prepared by heating white marble or better Iceland-spar to redness in a perforated crucible, when it splits up into carbonic anhydride, which escapes, and calcium monoxide, which remains behind—

$$Ca\,C\,O_3 = Ca\,O + C\,O_2.$$

Unless provision is made for the displacement of the carbonic anhydride evolved, complete decomposition does not take place.

2. By heating nitrate of calcium to redness in a crucible.

Manufacture.—Quicklime, as the monoxide of calcium is technically called, is made on a large scale by heating limestone in specially constructed furnaces (*lime-kilns*), which are generally egg-shaped. The lime so produced varies in quality, according to the nature of the limestone used; if containing an admixture of clay (argillaceous limestone) it is apt to vitrify, especially if overheated, or if containing magnesium carbonate (magnesian limestone), the lime produced will

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* Anglo-Saxon, *lim*, cement.

also contain magnesia (MgO), and under these circumstances the lime *slakes* badly—that is, it combines slowly and with little energy with water, and is termed *poor* lime, while if the lime be comparatively free from such admixtures, it combines immediately and with great energy with water, and is then termed *rich* or *fat* lime.

The *continuous process* of making lime is now largely used; it consists in a specially constructed kiln, into which alternate layers of limestone and small coal are introduced from the top, and the lime formed is from time to time removed through an opening in the side of its base.

Calcium Hydroxide (*calcium hydrate, hydrate of lime, slaked lime*), $Ca H_2 O_2 = 74$. $[Ca (H O)_2 ;\ Ca O, H_2 O]$. *Specific gravity*, 2·07 (*water* = 1).

Properties.—Calcium hydroxide is usually a white, impalpable powder; it may be obtained in crystals, but with difficulty. It is very sparingly soluble in water; much less soluble than the corresponding barium and strontium compounds, and more soluble in cold than in hot water. 100 parts of water dissolve 0·1368 quicklime at 15·6°, and 0·0752 part at 100°; or, in other words, quicklime requires for solution about 700 times its weight of water at ordinary temperatures, and about 1,200 times its weight at 100°. The solution (*lime-water*) has a strongly alkaline reaction and caustic taste, on exposure to air it quickly becomes coated with a pellicle of calcium carbonate due to its attraction for carbonic anhydride ($Ca O + C O_2 = Ca C O_3$). If carbonic anhydride is bubbled through lime-water, a precipitate of calcium carbonate is first produced, and after a time disappears, becoming dissolved in excess of the gas, but the clear solution so obtained becomes turbid again on boiling, the excess of carbonic anhydride being thus expelled. *Milk of lime* is a name given to a mixture of solid lime and water; it is much used for absorbing various gases in the laboratory, &c.

Solid calcium hydrate absorbs carbonic anhydride from the air, at first rapidly, but when half the lime has been converted into carbonate the absorption proceeds very slowly.

Calcium hydroxide at a red heat yields up its water, and is converted into quicklime.

Preparation.—1. By adding to quicklime about one-third of its weight of water.

Calcium Dioxide (*calcium peroxide*), $Ca O_2 = 72$. *Specific gravity*, 2·9 (*water* = 1).

A white crystalline powder having the composition, $Ca O_2, 8 H_2 O$, is precipitated when peroxide of hydrogen is added in excess to lime-water. It is efflorescent, and loses all its water at 130°, and at a somewhat higher temperature splits up into calcium monoxide and oxygen.

SALTS OF CALCIUM.

Calcium Carbonate, $Ca\,C\,O_3 = 100$.

Occurrence in Nature.—See calcium, p. 231.

Properties.—Calcium carbonate exhibits the phenomenon of allotropy in a most striking degree, and is dimorphous; as *calc-spar* it crystallises in forms (usually hemihedral) belonging to the hexagonal system, and as *arragonite* in forms belonging to the rhombic system. These two forms may be obtained artificially, the hexagonal form from cold solutions of calcium carbonate in water containing free carbonic anhydride, the rhombic form from similar hot solutions.

Calcium carbonate when precipitated by passing carbonic anhydride through lime-water, or by adding a solution of a carbonate of an alkali to a solution of a soluble calcium salt, is usually amorphous, but if slowly precipitated may be obtained crystalline. It is very sparingly soluble in water (1 part of the salt requiring about 55,000 times its weight of water for solution) unless free carbonic anhydride is present in the water; 100 parts of water saturated with carbonic anhydride dissolve 0·088 part of the salt at 10°. This solubility in water containing free carbonic anhydride accounts for its presence in natural waters (temporary hardness). It is precipitated from such solution by boiling, the carbonic anhydride being so expelled, or, but much more slowly, on standing (*cf.* calcium hydroxide, p. 233).

On heating to a red heat, under conditions in which the carbonic anhydride can escape, it breaks up into lime ($Ca\,O$) and carbonic anhydride ($C\,O_2$), a fact on which the preparation of lime is based (p. 232). If the carbonic anhydride is not allowed to escape partial decomposition only takes place (see dissociation, p. 76), and under sufficient pressure it can even be melted without decomposition.

Preparation.—1. By precipitating a solution of a calcium salt in water with a solution of a carbonate of an alkali. 2. By passing carbonic anhydride into lime-water, avoiding an excess.

Calcium Nitrate, $Ca(N\,O_3)_2, 4\,H_2\,O = 164 + 72 = 236$. $[(N\,O_2)_2\,.\,O_2\,Ca]$. *Specific gravity*, 1·85 (*water* = 1). *Melting point*, 44°; *of anhydrous*, 561°.

This salt is chiefly of interest owing to its occurrence as an efflorescence on the walls of stables, outhouses, &c., due to the oxidation of ammonia in the presence of lime (see also nitre, p. 207). It is very deliquescent, and very soluble in water.

Calcium Sulphate, $Ca\,S\,O_4,\ 2\,H_2\,O = 136 + 36 = 172.$ $[S\,O_2 \cdot O_2\,Ca]$. *Specific gravity*, 2·9 (*water* = 1).

Occurrence in Nature.—As already stated calcium sulphate occurs native, and when in large masses is known as *gypsum* or *alabaster*, or in monoclinic crystals as *selenite;* in all these forms it has the composition $Ca\,S\,O_4,\ 2\,H_2\,O$. More rarely it occurs in the anhydrous form in rhombic crystals, and is then called *anhydrite* ($Ca\,S\,O_4$).

Properties.—The hydrated salt is difficultly soluble in water, requiring about 400 times its weight for solution at ordinary temperatures, and is rather less soluble at higher temperatures. Gypsum on heating to 200° loses its water, and the anhydrous salt so formed, known as *burnt gypsum* or *plaster of Paris*, has the property of recombining with water, so that when mixed with not too much water it rapidly sets to a solid mass, with slight expansion of volume; it has on this account an extended use in the making of casts and as a cement. If heated much above 200° it no longer possesses this property.

The hydrated salt is soluble in hydrochloric and in nitric acid, from which solution it separates in crystals. It is soluble in concentrated sulphuric acid, with formation of an acid salt, $Ca\,(H\,S\,O_4)_2$, which is decomposed by water into the neutral salt and sulphuric acid. Boiled with a solution of an alkaline carbonate it is decomposed with formation of an alkaline sulphate and calcium carbonate.

Preparation.—The anhydrous salt is precipitated when dilute sulphuric acid is added to a solution of calcium chloride.

Sulphides of Calcium, *Monosulphide of calcium*, $Ca\,S$, is formed by the reduction of calcium sulphate with charcoal; it is a white infusible powder; after exposure to sunlight or magnesium light it phosphoresces in the dark (Canton's Phosphorus). It is practically insoluble in water, but on long boiling with water is gradually converted into *sulphydrate*, $Ca\,(S\,H)_2$. When lime and sulphur are heated together, or when milk of lime is boiled with flowers of sulphur, a number of higher sulphides (*polysulphides*) of calcium are formed, but they are with difficulty obtained pure (*cf. milk of sulphur*, p. 155, and *hydrogen persulphide*, p. 166). The *pentasulphide*, $Ca\,S_5$, and *tetrasulphide*, $Ca\,S_4$, are best known.

Calcium Chloride, $Ca\,Cl_2,\ 6\,H_2\,O = 111 + 108 = 219.$ *Specific gravity*, 1·68 (*water* = 1). *Melting point*, 28·5°; *of anhydrous*, 719°.

Properties.—This salt crystallises in colourless, exceedingly deliquescent hexagonal prisms, containing 49·3 per cent. of water of crystallisation. The crystallised salt melts in its water of crystallisation at 28·5°; if heated to 200° it loses 4 molecules of water, forming a dry porous mass, which is very deliquescent, and much used as a dessicating agent in the laboratory; at a higher temperature it becomes anhydrous, and at a red heat the anhydrous salt fuses with slight decomposition, yielding a crystalline mass on cooling.

Both the hydrated and anhydrous salts are very soluble in water, with considerable evolution of heat. The hydrated salt is soluble in one-quarter its weight of water at 16°, 100 parts of water dissolve 63·35 of the anhydrous salt at 10°, 120·48 at 40°. A solution containing 50 per cent. of the anhydrous salt boils at 112°, 200 per cent. 158°, 325 per cent. 180°. A mixture of equal parts of the hydrated salt and snow lowers the temperature to $-45°$.

With ammonia it forms a compound, whose formula is $CaCl_2, 8NH_3$; hence, it cannot be used for the drying of ammonia gas. It also yields a crystallised compound with alcohol, in which the latter replaces the water of crystallisation of the hydrated salt.

Preparation.—By solution of calcium carbonate in hydrochloric acid. Obtained as a by-product in the manufacture of ammonia from chloride of ammonium and lime.

Phosphates of Calcium, *Neutral or tricalcic orthophosphate,* $Ca_3(PO_4)_2$, occurs in nature associated with calcium fluoride in apatite [$CaF_2, 3Ca_3(PO_4)_2$], &c., and is a constituent of soils, of plants, and is the main mineral constituent of bones; it is present also in *guano.* It is insoluble in water, but soluble in nearly all acids, and even in a solution of carbonic anhydride (carbonic acid). It is soluble in water containing certain other salts in solution. It may be prepared by precipitating a solution of disodic hydrogen phosphate (Na_2HPO_4) with a solution of calcium chloride in the presence of a small quantity of ammonia.

Two other orthophosphates are known, viz.:—*Monohydrogen calcium orthophosphate* ($CaHPO_4$), and *tetrahydrogen calcium orthophosphate* (superphosphate) $CaH_4(PO_4)_2$ (see p. 191); the pyrophosphate, $Ca_2P_2O_7$, and metaphosphate, $Ca(PO_3)_2$, are also known.

Distinguishing Characters of Calcium Salts.—Calcium salts are colourless unless the acid is coloured; of the more common salts the carbonate and neutral phosphate are insoluble and the sulphate only slightly soluble in water.

Solutions of calcium salts give no precipitate with *calcium sulphate,* and, unless concentrated no precipitate with *sulphuric acid,* they yield a precipitate of calcium carbonate ($CaCO_3$) with *ammonium carbonate,* and even in dilute solutions yield a precipitate of oxalate of calcium (CaC_2O_4) with *oxalic acid* or *ammonium oxalate,* insoluble in ammonia or in acetic or oxalic acid; they yield no precipitate with hydrofluosilicic acid nor with potassium chromate (distinctions from barium and strontium).

Calcium salts in the solid state, especially when moistened with strong hydrochloric acid, impart a yellowish-red colour to the flame of a Bunsen burner, the spectrum of which is characterised by several bands in the green, yellow, and orange, of which one in the green and one in the orange are particularly brilliant.

Physiological Action.—The calcium salts are not poisonous; precipitated calcium carbonate is used in medicine as an antacid, and lime-water is also employed as an antacid and astringent.

MAGNESIUM.*

Mg=24. *Specific gravity*, 1·743 (*water*=1). *Specific heat*, 0·25. *Melts and volatilises at a red heat. Dyad.*

Occurrence in Nature.—Magnesium occurs very abundantly and widely diffused in nature. It is found in greatest quantity associated with calcium in *dolomite* ($Mg\,C\,O_3$, $Ca\,C\,O_3$) as carbonate; in this form it also occurs pure in *magnesite* ($Mg\,C\,O_3$); it is found as *sulphate* in *kieserite* ($MgSO_4$, H_2O) and *Epsom salt* ($MgSO_4$, $7\,H_2O$) and in *kainite* ($Mg\,S\,O_4$, $K\,Cl$, $6\,H_2O$); as *chloride* in *carnallite* ($Mg\,Cl_2$, $K\,Cl$, $6\,H_2O$) and *tachydrite* ($2\,Mg\,Cl_2$, $Ca\,Cl_2$, $12\,H_2O$); as *aluminate* in *spinelle* ($Mg\,O$, $Al_2\,O_3$); and as *silicate* in an immense number of minerals—*e.g.*, *asbestos*, *meerschaum*, *talc*, &c. (see magnesic silicates, p. 150). It is found as sulphate and as chloride in sea water and many mineral waters; many of its salts occur in the animal and vegetable kingdom (especially phosphates) and are constituents of soils.

Properties.—Magnesium is a silver-white metal; it is malleable, but scarcely ductile, and is made into wire and ribbon by pressing while hot; it melts at a red heat, and may be distilled. It preserves its lustre in dry air, but becomes coated with a very thin film of oxide in moist air. Heated strongly in contact with air it takes fire and burns with an exceedingly brilliant flame, which yields a continuous spectrum, and

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* At the beginning of the 18th century a panacea was sold by an ecclesiastic at Rome under the name of *Magnesia alba*, or the Count of Palma's Powder, and containing what we now call magnesia; the name was given, for no apparent reason whatever, in contradistinction to *Magnesia nigra*, a term which had been long applied to the mineral pyrolusite (now known as black oxide of manganese) on account of its colour and supposed magnetic properties; the circumstance gave rise, later on, to much confusion in the names of the respective metals contained in these two substances, and when, in 1774, *Magnesia nigra* was shown to contain a new metal, this was called *magnesium* by some, and *manganesium* (to avoid confusion) by others—the last being finally adopted, while *Magnesium* was retained for the metal of *Magnesia alba*.

is rich in *actinic*[*] or chemical rays, so that it is possible to make use of it as an artificial light in photography. A wire of 0·33 millimetre in diameter in burning produces a light equal to that of 74 stearin candles (five to the pound). It is used for purposes of powerful illumination, and special lamps have been constructed, in which, by means of clockwork, a piece of wire or ribbon is kept constantly in contact with the flame of a spirit lamp.

The product of its combustion is the oxide (MgO). It does not decompose water at ordinary temperatures, but begins to act upon it at 30°, and at 100° decomposes it energetically. It is soluble in dilute acids with evolution of hydrogen, but is scarcely acted on by sulphuric acid.

Preparation and Manufacture.—1. By the electrolysis of the fused chloride; or better, of a mixture of magnesium chloride, potassium chloride, and a little ammonium chloride; or fused *carnallite*, may be used.

2. The metal is now manufactured by acting on a mixture of fused magnesium and potassium chlorides (kieserite must not be present, or an explosion may occur) and fluor-spar with metallic sodium in a crucible at a red heat; a violent reaction occurs, and by stirring the contents of the crucible with an iron rod the magnesium is obtained in large globules. The crude metal is afterwards distilled in a special apparatus.

OXIDE OF MAGNESIUM.

Magnesium Oxide (*magnesia*, *magnesia calcinata or usta*, *bitter earth*, *talc earth*), $MgO = 40$. *Specific gravity*, 2·3 *to* 3·2 (*water* = 1).

Properties.—A light, white, tasteless powder; it slowly attracts water and carbonic anhydride from the air. It is practically insoluble in water, requiring 55,000 times its weight of water for solution. It has a feebly alkaline reaction to test paper when moistened with water. It is infusible, except at the highest temperatures. On long heating, it increases in specific gravity.

It forms a hydrate, $Mg(HO)_2$, or MgO, H_2O, which parts with its water when heated above 100°.

Physiological Action.—It is used as an antidote in cases of poisoning by arsenic, as an antacid and mild purgative.

Preparation and Formation.—1. Usually by igniting the carbonate, the *magnesia alba* of pharmacy. 2. By burning the metal in air.

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[*] *'ακτίς, a ray of light.*

SALTS OF MAGNESIUM.

Magnesium Carbonates.—The normal carbonate is found in the mineral *magnesite* ($Mg C O_3$) in rhombohedral crystals resembling those of calc-spar; specific gravity, 2·88 to 3·02.

The carbonate, which is precipitated by addition of a solution carbonate to a solution of a magnesium salt, is a basic carbonate of varying composition, according to temperature and strength of the solutions employed, and is distinguished, also, as *light* carbonate and *heavy* carbonate, according to its density, which is also dependent upon its mode of preparation. The *magnesia alba* of pharmacy has approximately the formula, $3 Mg C O_3, Mg O, 5 H_2 O$; it is very slightly soluble in water, but readily soluble in solutions of ammonium salts and in an aqueous solution of carbonic anhydride, especially under pressure.

Magnesium carbonate has been obtained in crystals corresponding both to *calc-spar* and *arragonite;* it is, therefore, isodimorphous with calcium carbonate.

Magnesium Nitrate, $Mg (N O_3)_2, 6 H_2 O = 148 + 108 = 256$. $[(N O_2)_2 . O_2 Mg]$. *Specific gravity*, 1·46 (*water* = 1). *Melting point*, 90°.

Properties.—This salt crystallises in rhombic prisms; it is extremely deliquescent, and very soluble in water. On heating, it first loses its water of crystallisation and is finally decomposed, only magnesium oxide remaining.

Preparation.—By dissolving magnesium carbonate in nitric acid, and evaporating the solution to crystallisation.

Magnesium Sulphate, $Mg S O_4, 7 H_2 O = 120 + 126 = 246$. $[SO_2 . O_2 Mg]$. *Specific gravity*, 1·7 (*water* = 1). *Melting point*, 70°; *anhydrous melts at a red heat.*

Occurrence in Nature.—The sulphate containing 7 molecules of water is found in solution in many mineral waters, and is generally known as *Epsom salt; kieserite* ($Mg S O_4, H_2 O$) contains only 1 molecule of water, and is found in various salt deposits.

Properties.—*Kieserite* is difficultly soluble in water. *Epsom salt*, on the contrary, is extremely soluble, requiring about an equal weight of water for solution at ordinary temperatures, and much less at higher temperatures; it easily forms supersaturated solutions (p. 107). The salt has a bitter taste; heated to 150°, it loses 6 molecules of water (*water of crystallisation*), but only parts with the seventh molecule at 250° (*water of constitution*). It is isomorphous with zinc sulphate, &c., crystallising in rhombic prisms. It can be obtained in monoclinic prisms. Magnesium sulphate can also be obtained crystallised with

2, 5, 6, and 12 molecules of water. It forms a very characteristic series of double salts with the sulphates of the alkalies, which have the general formula, $MgSO_4, M_2SO_4, 6H_2O$, and are isomorphous, crystallising in monoclinic prisms.

Physiological Action.—It is a powerful saline purgative.

Preparation.—1. From *dolomite* by the action of sulphuric acid, the calcium sulphate, being less soluble, separates out. 2. From *kieserite*, which is first treated with water to dissolve out the common salt with which it is usually contaminated.

Magnesium Chloride, $MgCl_2$, $6H_2O = 95 + 108 = 203$. *Specific gravity*, 1·56 (*water* = 1). *Melting point of anhydrous*, 708°.

Properties.—This salt may be obtained crystallised in needles with 6 molecules of water. When anhydrous, it is a white, crystalline, excessively deliquescent mass, which has a bitter taste. It is very soluble in water. The solution, on evaporation, especially when concentrated, decomposes into free hydrochloric acid, which escapes, and magnesia. This decomposition is prevented by the addition of ammonium chloride, with which it forms a double salt, the solution of which may be evaporated to dryness without loss of hydrochloric acid; and, if heated to 450°, yields up the volatile ammonium chloride, leaving anhydrous magnesium chloride.

It has marked antiseptic properties, and is largely used in dressing cotton.

Preparation.—By neutralising equal quantities of hydrochloric acid solution with magnesia and ammonia respectively, mixing the solutions, evaporating to dryness, and finally heating to 450° (see above).

Magnesium Phosphates.—*Trimagnesic phosphate*, $Mg_3(PO_4)_2$, exists in cereals and in bones, but in small quantity; several other phosphates may be prepared—they are all more or less difficultly soluble in water, but soluble in acids.

Ammonio-magnesium phosphate, $MgNH_4PO_4, 6H_2O$, is precipitated when a solution of disodic hydric phosphate is added to a clear solution of a magnesium salt containing ammonium chloride and free ammonia. It is very slightly soluble in water (1 in 15,000), and still less so in the presence of free ammonia (1 in 44,000). Heated to 100° it loses 5 molecules of water, but at higher temperatures it loses all its water and ammonia, and is converted into *magnesium pyrophosphate*, $Mg_2P_2O_7$; this compound is often selected for the quantitative estimation of magnesia and phosphoric acid. It is found in urinary calculus, and as a urinary deposit, frequently in very perfect crystals.

Distinguishing Characters of Magnesium Salts.—Magnesium salts are colourless, unless the acid is coloured, and are usually isomorphous with zinc, nickel, cobalt, cupric, and ferrous salts.

Solutions of magnesium salts give, with solutions of *caustic alkalies*, a white precipitate of magnesia hydrate ($Mg\,H_2\,O_2$) insoluble in excess, soluble in ammonium chloride and in alkaline citrates; a white precipitate with sodium and potassium carbonate solution, but not with a solution of ammonium carbonate in the cold; and solutions containing ammonium chloride and ammonia give a white crystalline precipitate ($Mg\,N\,H_4\,P\,O_4,\ 6\,H_2\,O$) with *disodic hydric phosphate*, which appears either immediately or on standing.

Physiological Action.—All magnesium salts act more or less as purgatives.

METALS OF THE EARTHS.

ALUMINIUM.
BERYLLIUM.
GALLIUM.
INDIUM.
CERIUM.
LANTHANUM.
DIDYMIUM.
YTTRIUM.
ERBIUM.
TERBIUM
YTTERBIUM.
DECIPIUM.
SAMARIUM.
SCANDIUM.

ALUMINIUM.*

Al = 27·5. *Specific gravity*, 2·67 (*water* = 1). *Specific heat*, 0·2143.
Melting point about 700.° *Pseudo-triad.*

Occurrence in Nature.—Aluminium is one of the most abundant and most widely diffused of the elements, but it is never found in the free state; it occurs chiefly as *silicate* and *oxide*.

In the form of silicate, it is a constituent of an enormous number of minerals and rocks, *e.g.*, the *felspars*, among which have already been mentioned *orthoclase* ($K_2\,Al_2\,Si_6\,O_8$), *leucite* ($K_2\,Al_2\,Si_4\,O_{12}$), *sodalite* ($2\,Na\,Cl,\ 3\,Na_2\,Al_2\,Si_2\,O_8$), and *albite* ($Na_2\,Al_2\,Si_6\,O_{16}$). The various felspars and the various *micas* (also aluminic silicates), together with quartz, &c., constitute the primary rocks such as *granite*, *gneiss*, *syenite*, *porphyry*, &c., and mica is also a constituent of *slate*. The felspars by natural disintegration give rise to the various *clays*, the purest forms of which, such as *kaolin*, or *white china clay*, *pipe-clay*, *Fuller's earth*, &c.,

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* So called in allusion to the fact that it is a constituent of *alumen* or alum.

correspond more or less to the composition, $Al_2O_3, 2SiO_2, 2H_2O$, while *marl*, *loam*, &c., are clays containing various admixtures, such as calcium carbonate, oxides of iron and magnesium, &c.

Among other aluminic silicates of interest may be mentioned the various *garnets*, including the *precious garnet*, which are silicates of aluminium, calcium, magnesium, and iron; *topaz*, a silicate of aluminium containing fluorine; *beryl* and *emerald* ($Be_3Al_2Si_6O_{18}$), and the splendid blue mineral known as *lapis lazuli*, a silicate of aluminium and sodium containing sulphur, probably in the form of a sulphide.

As anhydrous oxide (Al_2O_3) crystallised in hexagonal prisms, it forms, when colourless or grey, or dark coloured and opaque, the mineral *corundum*, next in hardness to the diamond; in a massive form and of a dark colour it is called *emery*, also much prized on account of its hardness; other crystalline and rarer varieties are the *sapphire*, of a blue colour said to be due to cobalt, the *oriental ruby* of a red colour, due to chromium, the *oriental topaz* (yellow), the *oriental amethyst* (purple), and the *oriental emerald* (green).

As hydrated oxide it constitutes the minerals *hydrargillite* (Al_2O_3 $3H_2O$), *bauxite* ($Al_2O_3, 2H_2O$), which also contains iron, and *diaspore* ($Al_2O_3 . H_2O$); as aluminate, it is found in *spinelle* (MgO, Al_2O_3), in *garnite* (ZnO, Al_2O_3), and in *chrysoberyl* (BeO, Al_2O_3).

Cryolite ($AlF_3 . 3NaF$) is another of the many forms of occurrence of this abundant and widely diffused element; it is also found as *sulphate* in some volcanic rocks, and as *phosphate* in *wavellite* and *oriental turquoise*.

Although the basis of all cultivated soils is an aluminic silicate, the compounds of aluminium enter in a subordinate degree only into the composition of vegetable matter grown on such soils, and hence also play a very subordinate part in the animal economy.

Properties.—Aluminium is a white metal, with a tinge of blue; it is extremely ductile and malleable, and possesses a bright metallic lustre. The metal is permanent in air at ordinary temperatures, and a compact piece oxidises but very slowly, even at a red heat; in thin leaves, however, it readily takes fire, and burns to oxide (Al_2O_3). When pure it does not decompose water, even at a red heat. It is soluble in hydrochloric and sulphuric acids, with evolution of hydrogen, but is not acted on by nitric acid. The metal is also soluble in caustic alkalies, with evolution of hydrogen.

Aluminium is the lightest of those metals which are sufficiently permanent in air to allow of their use as metals, and as it possesses at the same time great tenacity, it is used for purposes for which lightness and tenacity are of value, as in beams of delicate balances, optical instruments, &c. It also forms several useful alloys distinguished for strength, lightness, and colour. *Aluminium bronze* is an alloy of 90 parts of copper and 10 parts of aluminium; it has the colour of gold, and has twice the tenacity of gun-metal.

Preparation.—1. By heating either the chloride of aluminium ($Al_2 Cl_6$) or the double chloride of aluminium and sodium ($Al_2 Cl_6$, $2 Na Cl$), or the fluoride of aluminium and sodium ($Al F_3$, $3 Na F$), with metallic sodium, in a crucible or on the hearth of a reverberatory furnace. 2. By the electrolytic decomposition of a fused mixture of the chlorides of aluminium and sodium.

OXIDE OF ALUMINIUM.

Aluminium forms but one compound with oxygen called *Alumina.*

Alumina, $Al_2 O_3 = 93$. *Specific gravity*, 3·9 (*water* = 1).

Occurrence in Nature (see *Aluminium*, p. 242).

Properties.—*Crystallised* in the hexagonal system it constitutes, according to its colour, various precious stones (p. 242); these have also been prepared artificially; in this form it is, next to diamond and boron, the hardest of all known substances, and is insoluble in acids; *amorphous*, it constitutes a white powder, which is soluble in acids when prepared at a low temperature, but which is almost insoluble after it has been strongly heated. It is fusible only in the oxyhydrogen blowpipe. Fused with caustic alkalies it yields compounds which are soluble in water (*aluminates*).

Preparation.—Of *crystallised*, by the action of boric anhydride on fluoride of aluminium at a very high temperature; or by heating together fluoride of barium and alumina; of *amorphous*, by heating either hydrate of alumina or ammonia alum.

Hydrates of Alumina.—Various hydrates of alumina are known. The gelatinous precipitate produced in solutions of aluminium salts by the addition of ammonia has, after drying at ordinary temperature, the composition $Al_2 H_{10} O_8 = Al_2 O_3 5 H_2 O$; when dried at a little over 300° it loses 4 molecules of water, and becomes $Al_2 O_3$, $H_2 O$, a hydrate which is also found native, as the mineral *diaspore*. Two other hydrates of the composition, $Al_2 O_3 3 H_2 O$ and $Al_2 O_3 2 H_2 O$, are also found native, as the minerals *hydrargillite* and *bauxite* respectively. Freshly precipitated hydrate of alumina is readily soluble in acids, and also in caustic alkalies, but becomes more difficultly soluble after standing for some time. The freshly precipitated hydrate also dissolves in a solution of chloride of aluminium, and when this solution is subjected to dialysis the chloride passes out, leaving aluminic hydrate dissolved in water in the dialyser; the solution, like the corresponding solution of iron, is very unstable (see *dialysed iron*, p. 277).

Alumina acts as a feeble basic oxide in contact with strong acids, but behaves like a feeble acid in contact with strong bases, forming compounds termed *aluminates*. Several of these compounds are found native, such as the minerals *chrysoberyl*, Al_2O_3BeO, and *spinelle*, Al_2O_3MgO; some like the aluminate of potassium, $Al_2O_3, K_2O, 3H_2O$, may be obtained crystallised by evaporating a solution of alumina in caustic potash *in vacuo*. The corresponding sodium compound has not been obtained in the crystalline form, but its solution is used as a *mordant*.*

SALTS OF ALUMINIUM.

Aluminium forms no carbonate.

Nitrate of Aluminium, $Al_2(NO_3)_6, 18H_2O. = 427 + 324 = 751.$

This salt is obtained by dissolving the hydrate in nitric acid. It is employed as a mordant in calico printing. It crystallises in deliquescent needles.

Sulphate of Aluminium, $Al_2(SO_4)_3, 18H_2O = 343 + 324 = 667$. *Specific gravity*, 1·6 (*water* = 1).

This salt is found native, as the mineral *keramohalite*, and is prepared on a large scale by dissolving hydrate of alumina in sulphuric acid, or by decomposing China clay ($Al_2O_3, 2SiO_2, 2H_2O$) by sulphuric acid and evaporating the solution, or by the spontaneous oxidation of alum shale (245). The salt is soluble in twice its weight of cold water, and crystallises with difficulty. It is used as a mordant and for weighting paper.

Basic sulphates may be obtained by boiling the solution of the sulphate with freshly precipitated hydrate, or precipitating it with an insufficient quantity of ammonia.

Alums.—One of the most characteristic properties of the sulphate of alumina is the ease with which it forms double salts, known as *alums*, with the sulphates of the alkalies. Originally the name of alum was applied to the double sulphate of aluminium and potassium, but it is now

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* Aluminic hydrate has a strong affinity for certain colouring-matters, and is therefore employed as a means of fixing these on fibres which have no direct affinity for such colouring-matters; in such case the alumina is said to act as a mordant.

applied to double sulphates of all oxides isomeric with these. Alum is used extensively in calico printing and dyeing, for which purposes it must be as pure as possible, and especially free from iron.

Alum (*potash alum*, *common alum*), $Al_2\,K_2\,(S\,O_4)_4\;24\,H_2\,O = 517 + 432 = 949$. $[Al_2\,(S\,O_4)_3,\;K_2\,S\,O_4,\;24\,H_2\,O]$. *Specific gravity*, 1·72 (*water* = 1). *Melting point*, 84·5.

Properties.—This salt crystallises in large transparent, regular octahedra, soluble in seven parts of water at 20°, and in less than one-third of their weight at 100°. When heated the crystals at first melt in their water of crystallisation, which, on continuous heating, is expelled, leaving a white porous mass known as burnt alum. The solution has a slightly acid reaction and a powerfully astringent sweetish taste.

Physiological Action.—It is used as an astringent for local application and internal use; as a mild caustic in the form of burnt alum.

Preparation.—1. By roasting alum-stone (*alumite*), a native basic sulphate of alumina and potash, found near Tolfa in Italy, and Muzsai in Hungary, exposing the roasted mass to the action of the air, and finally extracting with water, when alumina remains behind, while alum goes into solution.

$$\overset{\text{Alum-Stone.}}{K_2\,S\,O_4,\;3\,Al_2\,S\,O_6,^{*}\;6\,H_2\,O} - \overset{\text{Aluminic Hydrate.}}{2\,(Al_2\,O_3,\;3\,H_2\,O)} = \overset{\text{Alum.}}{K_2\,S\,O_4\,Al_2\,3\,S\,O_4}.$$

The alum so prepared is known as *Roman alum.*

2. By mixing, in proper proportion, solutions of sulphate of alumina and sulphate of potassium, or chloride of potassium and sulphuric acid, and crystallising.

3. By gently roasting *alum-shale* (a bituminous silicate of alumina containing iron pyrites), and then exposing it, moistened, to the action of the air. The ferrous sulphide is oxidised, yielding ferrous sulphate and sulphuric acid, which latter, acting on the silicate of alumina, yields sulphate of alumina. The shale is then extracted with water, as much as possible of the iron separated by crystallisation, and the solution of sulphate of aluminium mixed with potassium sulphate, and allowed to crystallise. Any iron which had not been separated by crystallisation may be prevented from crystallising with the alum by the addition of an equivalent proportion of chloride of potassium, which yields sulphate of potassium and chloride of iron; the latter remains in solution.

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[*] The basic sulphate of alumina may be regarded as a salt of hexabasic sulphuric acid, $H_6\,S\,O_6$, corresponding to the salt which remains behind when sulphate of iron is heated to a moderate degree (see *Manufacture of Nordhausen Sulphuric Acid*, p. 162).

As before stated, the two metals present in this alum (common alum) may be replaced by isomorphous metals, with formation of compounds perfectly analogous to this common alum, and crystallising like this in regular octahedra. The general formula of these isomorphous compounds, to which the name of alums has been extended, may be given as follows:—

$$M_2'SO_4, M_2'''(SO_4)_3 + 24H_2O,$$

where M′ and M‴ stand for the metals replacing potassium and aluminium respectively. Thus the potassium may be replaced by cæsium, rubidium, sodium, or ammonium, the latter being generally present in ordinary English alum, while the alumina may be replaced by iron, chromium, or manganese, and a great variety of alums known as *ammonia alum*, *chromium alum*, *iron alum*, &c., are thereby produced.

Chloride of Aluminium (*aluminic chloride*), $Al_2Cl_6 = 268$. *Specific gravity of vapour*, 134 ($H = 1$).

Properties.—This salt crystallises in colourless and transparent, or white and opaque, crystals belonging to the hexagonal system; the salt may, by heating, be readily sublimed without previous fusion, but may be fused under slightly increased pressure. When free from moisture, it may be heated without decomposition; but in presence of water it breaks up, when heated, into alumina and hydrochloric acid; exposed to the action of moist air, it deliquesces, and gives off fumes of hydrochloric acid. It is soluble in water, and may be obtained from its solution in colourless needle-shaped crystals of the composition, $Al_2Cl_6, 12H_2O$. The same crystals are obtained by evaporating the solution of the metal or of alumina in hydrochloric acid to crystallisation.

Preparation.—By passing chlorine over a strongly heated mixture of alumina and powdered charcoal, or coal, contained in a porcelain tube or fire-clay retort.

The *double chloride of aluminium and sodium*, used in the preparation of the metal, is obtained by the addition of chloride of sodium to a mixture of alumina and charcoal, and heating to a white heat in a current of chlorine. The double salt volatilises, and is condensed in suitable vessels. This double chloride is less volatile, but more fusible, than aluminium chloride, and being less readily acted on by moist air, it is now always used in the preparation of aluminium.

Phosphate of Aluminium, $Al_2(PO_4)_2 = 245$.

This salt is obtained as a gelatinous hydrate by the addition of phosphate of soda to a neutral solution of an aluminium salt. The precipitate is soluble in caustic alkalies and in mineral acids, insoluble in ammonia and in acetic acid. Several basic phosphates are found native—*e.g.*, *wavellite* [$2\,Al_2\,(P\,O_4)_2, Al_2\,O_3, 3\,H_2\,O$] and *oriental turquoise*.

Aluminium Sulphide, $Al_2\,S_3 = 151$.

This salt is obtained as a black mass by heating aluminium and sulphur together to a red heat, or as a white substance by passing the vapour of bisulphide of carbon over aluminium heated to a white heat. It is decomposed by water into alumina and sulphuretted hydrogen, and cannot therefore be formed in the wet way.

Ultramarine.—This is the double silicate of alumina and soda containing sulphur in the form of a sulphide, which occurs native as *lapis lazuli*, but for which no definite formula has been found. The commercial product in imitation of the natural one, and obtained by heating together clay, soda, sulphur, and charcoal, in various proportions, is at first white, but speedily turns green (green ultramarine), and when this is heated with sulphur in presence of air, it becomes blue without change of composition. Ultramarine is not acted on by alkalies, but is readily decolorised by acids with evolution of sulphuretted hydrogen.

General Characters of Aluminium Compounds.—The compounds of aluminium are colourless, if the acid is colourless ; they have a sweet and very astringent taste, and an acid reaction. Caustic alkalies, and their carbonates and sulphides, precipitate aluminic hydrate; the gelatinous precipitate is soluble in caustic alkalies, but scarcely soluble in ammonia. When heated, after moistening with nitrate of cobalt, before the blowpipe a blue mass is produced (Thénard's blue). Aluminium salts do not colour the flame of a Bunsen burner.

Physiological Action.—(See *Alum*, p. 245.)

Glass, Porcelain, Stoneware, Earthenware.—**Glass** is essentially a double silicate of potassium or sodium and of calcium or lead, which has the property of solidifying in the vitreous condition, and which, when heated, passes through a stage of greater or less softness (viscosity) before it actually melts. During this stage of softness it can be brought into any desired shape, and two or more pieces can be *welded* or joined together so as to form one homogeneous piece. The chief varieties of glass are :—

1. *Bohemian or potash glass*, a potassium-calcium silicate.
2. *Crown glass* (*window glass*, *plate glass*), a sodium-calcium silicate.
3. *Flint glass*, a potassium-lead silicate.
4. *Bottle glass*, an impure crown glass, consisting of sodium, calcium, aluminium, and iron silicates.

The first three varieties are colourless,* or nearly so, the last is more or less deeply coloured. The first is less fusible, and resists the action of chemical agents better than the others, while the third is chiefly remarkable on account of its high dispersive power for light and consequent brilliancy, which property increases with the increase in the proportion of lead present (optical glass, *strass*).

Speaking generally, a glass melts the more readily, and is the more easily acted on by chemical agents, the more alkali it contains, and is the less fusible and the less readily acted on when the alkaline earth predominates. A calcium glass containing too much silica is very apt to crystallise when kept hot for a short time and then becomes opaque, or devitrified. A potash glass is, under otherwise similar conditions, less fusible than a soda glass.

After glass has been melted, or even only strongly heated, it has to be passed through a process of very slow cooling (*annealing*), otherwise it is liable to fracture by changes of temperature, or by very slight injury, owing to internal strains or tension due to irregular cooling.

Composition of Samples of the Four Chief Varieties of Glass.

	Bohemian glass.	Crown glass.	Flint glass.	Bottle glass.
SiO_2	71·7	76·0	51·93	59·6
K_2O	12·7	...	13·67	...
Na_2O	2·5	17·0	...	3·2
CaO	10·3	6·0	...	18·0
MgO	...	...	...	7·0
MnO	0·2	...	...	0·4
Al_2O_3	0·4	...	...	6·8
Fe_2O_3	0·3	1·0	...	4·4
PbO	...	...	33·28	...

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* The green colour due to the presence of ferrous oxide contained in almost all the materials used in the manufacture of glass may be counteracted by the addition of oxide of manganese, which by itself would impart a rose tint to the glass. This rose tint is exactly complementary to the green of the ferrous oxide, and the two complementary colours neutralise each other, and so render the glass colourless.

Coloured glass is produced by the addition of various metallic oxides which, dissolving in the melted glass, impart to it a characteristic colour. Thus red glass is produced by the addition of cuprous oxide or of purple of Cassius; blue, by oxide of cobalt; violet, by manganese, green, by cupric, chromic, or ferrous oxide; yellow, by antimonic or ferric oxide; yellowish-green, with a strong fluorescence by uranium.

In some cases the whole mass of the glass is coloured, in other cases, notably that of red glass, the colour is confined to a thin film on one surface of the glass only.

True **China** or hard **porcelain** is made from the purest *kaolin* ($Al_2 O_3$, $2 Si O_2$, $2 H_2 O$) mixed with a frit consisting of felspar, sand, and chalk, and glazed with a mixture, similar to that of the frit used. The kaolin by itself is infusible, even in the intense heat of the porcelain kiln, but the frit with which it is mixed melts, and penetrates the whole mass, rendering the otherwise porous and opaque material translucent and impervious. Hard porcelain is baked and glazed in one operation.

English or **soft porcelain** consists of kaolin mixed with a frit of bone-ash and borax, which is much more fusible than the frit used for hard porcelain. Soft porcelain is first baked (biscuit) and is then glazed with an easily fusible mixture of bone ash, oxide of lead, potash, sand, and borax.

Stoneware differs from porcelain chiefly in being made with less pure materials, and in that it is glazed by a process called salt-glazing. The articles to be glazed are dipped in a mixture of sand and water, and heated to a high temperature. Salt is thrown into the kiln; it volatilises, and is decomposed by the silica of the sand in presence of moisture, hydrochloric acid is evolved and a readily fusible silicate of soda formed, which combines with the silicates of the ware, and forms an impervious coating.

Earthenware differs from the two preceding, in the fact that no fusion of the material takes place during the firing, and that, therefore, the body of the ware remains porous; it is glazed when required with an opaque lead glass. It is generally made from more impure materials than either stoneware or porcelain.

Bricks, *flower-pots*, &c., are made from still more impure materials; their colour is due to the presence of ferric oxide.

Mortars and Cements.—*Mortar* is essentially a mixture of slaked lime ($Ca H_2 O_2$), with from three to four times its weight of sand ($Si O_2$); its hardening is chiefly due to the gradual conversion of the slaked lime into carbonate by absorption of carbonic anhydride (CO_2) from the air; this absorption is at first rapid, but gradually becomes slower, and, when half the lime is converted into carbonate, proceeds very slowly indeed. Mortars even centuries old still contain appreciable quantities of hydrate of lime. The hardening may be, in some cases, partially due to the formation of silicate of calcium.

The conversion of the hydrate of lime into carbonate is accompanied by the liberation of water, and it should be borne in mind that the water so separated is the result of chemical action, not the mere evaporation of moisture; hence the "sweating" of newly built or plastered walls. The method of drying such walls by means of charcoal fires is not a simple drying by heat, but essentially a chemical drying, since the carbonic anhydride evolved from the charcoal stoves is necessary to the process of dehydration.

Hydraulic mortars are made with limes containing from 15 to 30 per cent. of finely divided silica or clay, and these possess the property of hardening under water, with which they apparently enter into chemical combination. *Portland cement* is made by burning an intimate mixture of chalk and clay; the larger the proportion of clay the more rapidly do such cements harden—so-called *Roman cement*, for example, containing about 25 per cent. of clay, sets hard in a few hours.

BERYLLIUM.*

(*Glucinum* †) *Be* = 9·4. *Specific gravity*, 2·1 (*water* = 1). *Specific heat*, 0·4079. *Dyad.*‡

Occurrence in Nature.—This metal occurs in certain rare minerals; as silicate in *beryl* ($Be_3Al_2Si_6O_{18}$), the transparent green varieties of which constitute the precious stone *emerald*, those which have a bluish tint being called *aquamarine;* and in *phenacite* ($BeSiO_4$), &c.; as oxide in *chrysoberyl* (BeO, Al_2O_3), and as a minor constituent of many minerals.

Properties.—Beryllium is a silver-white metal; its melting point is somewhat below that of silver; it is malleable; it takes fire in air on strongly heating, but only if finely divided. It is soluble in dilute acids on warming.

Preparation.—By distilling the chloride over metallic sodium.

Oxides and Salts.—Beryllium only forms one oxide, BeO, which is a basic oxide, and which resembles alumina (Al_2O_3) in some respects, and magnesia (MgO) in others; it is a white powder, insoluble in water, but soluble in dilute acids, if it has not been previously

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* The metal contained in beryl. Latin, *beryllus;* Greek, *βήρυλλος*, *beryl.*

† The metal was at one time termed *glucinum* (γλυκύς, sweet), from the fact that some of its compounds have a sweet taste.

‡ Some chemists are of opinion that this element is a hexad like aluminium, that it has an atomic weight of 13·6, and that the formula of its oxide is therefore Be_2O_3; its specific heat points to the higher number—on the other hand, its analogy to magnesium points to the lower atomic weight as correct.

ignited; fused with fixed alkalies it forms soluble compounds; the hydrate, $Be(OH)_2$, is precipitated by alkalies from solutions of beryllium salts, and is soluble in excess of these precipitants, and also in ammonium carbonate solution (distinction from aluminium). It forms several salts which are white, unless the acid is coloured. A basic carbonate is deposited on boiling the solution of the hydroxide in ammonium carbonate. The chloride $BeCl_2$, the sulphate $BeSO_4$, and nitrate $Be(NO_3)_2$, are soluble in water.

Distinguishing Tests.—See behaviour of its oxide.

GALLIUM.*

Ga = 68. *Specific gravity*, 5·95 (*water* = 1). *Specific heat*, 0·080. *Melting point*, 30°.

Occurrence in Nature.—This extremely rare metal occurs in minute quantities in some *zinc blende* (ZnS), more especially in the valley of Argeles in the Pyrenees where it was first discovered.

Properties.—The existence of this metal was first indicated by its spectrum which is characterised by a violet line. It is a white metal, and has the remarkably low melting point of 30°, so that it melts when placed in the palm of the hand; once melted it remains liquid even when cooled below 0°, but solidifies when touched with a piece of solid gallium; it is not volatile, and oxidises but slightly in air when heated. It is soluble in acids and alkalies.

Preparation.—By the electrolysis of an alkaline solution of its sulphate. Its separation from zinc, which is a very tedious and difficult process, is effected by fractional precipitation of a boiling solution of the two metals with sodium carbonate, gallium carbonate being more easily precipitated.

Oxides and Salts.—Its oxide is white, and has presumably the formula, Ga_2O_3. Gallium sulphate forms an *alum* (p. 246) with ammonium sulphate, $Ga_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$. A chloride is also known.

Distinguishing Tests.—Its spectrum is characteristic (see also *Preparation*).

INDIUM.†

In = 113·4. *Specific gravity*, 7·42 (*water* = 1). *Specific heat*, 0·057. *Melting point*, 176°.

Occurrence in Nature.—This very rare metal was first observed in Freiberg accompanying *zinc blende* (ZnS) in minute quantities, and has been found in some other localities in the same mineral.

Properties.—Indium is a brilliant white metal, softer than lead, malleable, and melts at 176°. At a higher temperature it may be distilled, but is not so volatile as zinc or cadmium. It remains unaltered in air even when melted, but at a higher temperature takes fire and burns with a blue flame to oxide (In_2O_3). It is soluble in dilute acids; the hydrogen evolved burns with a blue flame. It is precipitated from its solutions by zinc and cadmium.

Preparation.—By reduction of the oxide with sodium. The metal is originally obtained in an impure form as a black precipitate, when Freiberg zinc is treated with an amount of hydrochloric acid insufficient to completely dissolve it. The impure metal is further purified by various complicated processes.

Oxides and Salts.—Indium forms a monoxide, InO, and a trioxide, In_2O_3, both basic. It forms an *alum* (p. 246), $In_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$, and a large number of its salts have been prepared.

Distinguishing Tests.—Indium and its salts impart a fine blue colour to the flame of a Bunsen burner, and yield a characteristic spectrum.

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* So called by its discoverer, Lecoq de Boisbaudran, in patriotic allusion to his country.

† So called in allusion to the blue line of its spectrum.

CERIUM, LANTHANUM AND DIDYMIUM.*

$Ce = 138$; $La = 139$; $Di = 144·75$.

These three metals occur intimately associated with one another in *cerite*, *orthite*, *gadolinite*, and some other very rare natural silicates first found in Norway and Sweden. Cerium was the first discovered (1804), and in its supposed oxide first lanthanum (1839), and later didymium (1843) were detected. The separation of these metals is a matter of the greatest difficulty, but perfectly pure and isolated preparations were obtained by Bunsen, with a view to determining their spectra. The method of separation, after removal of all commoner metals, depends upon the comparative insolubility of the basic sulphate of cerium, and the greater solubility of didymium sulphate as compared with lanthanum sulphate; all these metals form insoluble oxalates; they also form insoluble double sulphates with potassium sulphates, and use is made of this fact to separate them from yttrium and erbium.

They may all three be prepared in the metallic state by electrolysis of the chloride ($M\,Cl_3$). Cerium resembles iron in appearance, tarnishes rapidly in moist air, and takes fire very easily, burning with a more brilliant light than magnesium. Lanthanum and didymium possess similar properties. All three form a sesquioxide ($M_2\,O_3$), and a corresponding hydrate which absorbs carbonic anhydride from the air; cerium forms also a dioxide. A large number of their salts have been prepared.

Cerium and lanthanum salts yield very characteristic spectra; didymium salts are rose-red, and yield a remarkable *absorption spectrum*, which is a special and very delicate characteristic.

YTTRIUM, ERBIUM, TERBIUM, AND YTTERBIUM.†

$Y = 61·7$; $E = 112·6$; $Tr = 148·5$; $Yb = 172·8$.

These metals also occur in those silicates in which cerium, lanthanum, and didymium are found, but chiefly in *gadolinite;* the separation of yttrium and erbium from the above-mentioned metals has already been referred to above; their separation from one another is based on a difference in the solubility of their nitrates; erbium nitrate being the less soluble. They are not known in the free state, and closely resemble one another; they are characterised by special spectra; several salts of yttrium and erbium have been prepared.

DECIPIUM, SAMARIUM, SCANDIUM.

$Dp = 159$ (?); $Sm = 150$; $Sc = 44$.

These three metals are found associated with the metals didymium, erbium, and others of this group, and closely resemble them in general character and in the constitution of their oxides and chlorides.

Decipium was discovered by Delafontaine in the mineral *samarskite* found in N. Carolina. None of its compounds have yet been obtained in a state of purity, but their solutions are characterised by a special absorption spectrum.

Samarium was discovered by Lecoq de Boisbaudran in *samarskite*, and is easily recognised by its spectrum.

Scandium was discovered by Nilson in the minerals *gadolinite* and *euxenite*.

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* *Cerium*, named after the Planet Ceres then (1804) newly discovered; *lanthanum*, from λανθανω, I lie hid, in allusion to its having been overlooked in *cerite; didymium*, from διδυμος, *two-fold*, *twin*, in allusion to its intimate association with lanthanum.

† All these names are based on the name of the locality *Ytterby*, in Sweden, from which the minerals containing these metals were first derived.

HEAVY METALS.

ZINC.
CADMIUM.

LEAD.
THALLIUM.

MANGANESE.
IRON.
COBALT.
NICKEL.
CHROMIUM.
MOLYBDENUM.
TUNGSTEN.
URANIUM.

TIN.
TITANIUM.
ZIRCONIUM.
THORIUM.

BISMUTH.
NORWEGIUM.

ANTIMONY.
ARSENIC.
VANADIUM.
TANTALUM.
NIOBIUM.

COPPER.

ZINC.*

Zn = 65.† *Specific gravity*, 6·9 (*water* = 1). *Melting point*, 433°. *Boiling point*, 1040°. *Specific heat*, 0·095. *Dyad.*

Occurrence in Nature.—Zinc is found as oxide, sulphide, carbonate, and silicate in deposits in various parts of the world, notably in New Jersey, the United States, Belgium, Silesia, Spain, and Great Britain.

Its chief ores are *calamine*, also called *smithsonite*, *zinc-spar*, &c. ($Zn\,C\,O_3$); *zinc blende* ($Zn\,S$); *red zinc ore* ($Zn\,O$); and *siliceous calamine* ($Zn_2\,Si\,O_4,\ H_2\,O$). As sulphide it is frequently found associated with galena, and as carbonate with dolomite. It is mostly accompanied by cadmium in small quantities.

Properties.—Zinc is a moderately hard, bluish-white metal of crystalline structure; it is usually very brittle, but when heated to a temperature between 120° and 150° it is malleable, and retains its malleability on cooling; at 205° it becomes so brittle that it can be powdered in a mortar; at 433° it melts, and boils at 1040° (a bright red heat). If heated to redness, in contact with air, it takes fire, and burns with a brilliant bluish flame, forming zinc oxide ($Zn\,O$). It tarnishes slowly in contact with moist air, more rapidly in the presence of any acid, even carbonic acid. It decomposes water at a red heat. It is soluble in dilute hydrochloric and sulphuric acid, with evolution of hydrogen, and formation of chloride and sulphate of zinc respectively; nitric acid dissolves it, forming the nitrate, but is itself partially decomposed. Zinc is also soluble in solutions of the alkaline hydrates.

The metal is used in the form of sheet zinc chiefly. It is also used for protecting iron from rusting (galvanised iron); zinc and iron

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*The name *zinc*, German *zink*, is of uncertain origin; perhaps allied to *zinn*, tin, and meaning "tin-like."—*Skeat*.

†See p. 59.

forming a galvanic couple, in which the iron is the negative (unacted-on) metal; the galvanising is effected by dipping the thoroughly clean iron into molten zinc.

It is a constituent of many important alloys, among which may be mentioned *brass* (copper and zinc) and *German silver* (copper, zinc, and nickel).

Granulated zinc is zinc which has been melted and poured in a thin stream into water, by which process it is broken up into small, irregular lumps, which are useful for dissolving in acids, &c.

Zinc-dust is a finely divided form of zinc obtained in the manufacture of the metal; it is generally mixed with oxide, from which it may be freed by treatment with very dilute hydrochloric acid.

Manufacture.—The ores are first converted into oxide by careful roasting, mixed with charcoal, coke, or coal-dust, and subjected to distillation at a bright red heat in earthenware retorts. Commercial zinc is liable to contain arsenic, antimony, lead, &c.

OXIDE OF ZINC.

Zinc Oxide (*zinc-white*, *lana philosophica*, *nix alba*), $Zn\,O = 81$. *Specific gravity*, 5·6 (*water* = 1).

Occurrence in Nature.—As *spartalite* or red oxide of zinc in crystals of the hexagonal system; usually containing oxide of manganese.

Properties.—Zinc oxide is a white powder, very difficultly fusible; when hot it is yellow, becoming white again on cooling. It is a basic oxide, and is soluble in acids, forming a number of salts isomorphous with magnesium salts; it is, however, also soluble in solutions of the fixed alkalies.

It is used as a pigment, and has the advantage of not being discoloured by the action of hydrogen sulphide.

Preparation.—By burning the metal in air, or by heating the hydrate, carbonate, or nitrate.

Zinc Hydroxide (*hydrated oxide of zinc*), $Zn\,(H\,O)_2 = 99$. $[Zn\,O\,.\,H_2\,O]$.

This substance is precipitated white and flocculent when an insufficient amount of a solution of a caustic alkali is added to a solution of a zinc salt, but it is soluble in excess of the reagent, from which solution it may be obtained in crystals. It may be dried over chloride of calcium without loss of water of hydration, but becomes anhydrous when heated to redness.

SALTS OF ZINC.

Zinc Carbonate, $ZnCO_3 = 125$.

Occurrence in Nature (see Zinc).

Properties.—Native zinc carbonate crystallises in rhombohedra; it has a specific gravity of 4·42. The artificial carbonate may be obtained by precipitating a solution of sulphate of zinc with an excess of bicarbonate of potassium (not sodium). The hydrate retains some water even at 200°. Like the carbonates of barium, strontium and calcium, carbonate of zinc is readily soluble in water containing carbonic anhydride in solution. A hydrated basic carbonate is precipitated from solutions of zinc salts by a solution of sodium carbonate.

Zinc Nitrate, $Zn(NO_3)_2, 6H_2O = 189 + 108 = 297$. $[(NO_2)_2 . O_2Zn]$. *Melting point*, 36·4°.

A crystalline, very deliquescent salt, obtained by dissolving zinc in nitric acid; it forms, also, a less soluble basic nitrate.

Zinc Sulphate (*white vitriol*), $ZnSO_4, 7H_2O = 161 + 126 = 287$. $[SO_2 . O_2Zn]$. *Specific gravity*, 1·95 (*water* = 1). *Melting point*, 50°.

Properties.—This salt crystallises in rhombic prisms isomorphous with magnesium sulphate, which it much resembles in appearance—a fact which has led to fatal mistakes, the salt being poisonous. It has a metallic, astringent taste. It dissolves in about 2½ times its weight of cold water, and is still more soluble at higher temperatures. On heating, it behaves like magnesium sulphate, losing six molecules of water at a moderate heat, and the seventh only at a higher temperature.

Physiological Action.—It is used in medicine as an emetic.

Preparation.—1. By roasting the sulphide and dissolving and crystallising the product. 2. By dissolving zinc in dilute sulphuric acid and evaporating to crystallisation.

Zinc Sulphide (*blende, zinc blende*), $ZnS = 97$. *Specific gravity*, 4·0 (*water* = 1).

This salt is found native, crystallised in the regular system; when pure, it is light yellow, but is often darker and sometimes black (*black Jack*), owing to the presence of iron and other metals.

A white hydrated sulphide is precipitated on adding a solution of an alkaline sulphide to a solution of a zinc salt; it is soluble in dilute mineral acids, but not in acetic acid. Dried at ordinary temperatures, it has the composition, ZnS, H_2O; dried at 100°, $2ZnS, H_2O$.

Other sulphides are known, such as ZnS_5; $ZnS\ ZnO$; $4ZnS, ZnO$.

Zinc Chloride, $ZnCl_2 = 136$.

This salt may be obtained as a white, excessively deliquescent solid, by evaporating its solution sufficiently, or in crystals, having the composition $ZnCl_2, H_2O$, if strong hydrochloric acid is added to its concentrated solution. It melts at 100°, and sublimes at higher temperatures.

Its solution, like that of magnesium chloride, is apt to undergo decomposition on evaporation, hydrochloric acid being given off and a basic salt formed.

It is used as a caustic and as a desiccant, and is a powerful deodorant and antiseptic.*

Preparation.—1. By dissolving zinc, or zinc oxide, or carbonate in hydrochloric acid solution, and evaporating to a syrup. 2. By distilling a mixture of zinc sulphate and chloride of calcium. 3. By heating finely divided zinc with corrosive sublimate.

Distinguishing Characters of Zinc Salts.—Zinc salts are white, unless the acid is coloured.

Solutions of zinc salts yield, with solutions of *caustic alkalies* and with ammonia, a white precipitate of the hydrate $[Zn(HO)_2]$ soluble in excess; *sodium and potassium carbonate* solutions give a white precipitate of carbonate, insoluble in excess; ammonium carbonate the same precipitate, soluble in excess; *sulphuretted hydrogen*, a white precipitate of the hydrated sulphide in neutral or alkaline solutions; and *ammonium sulphide*, the same precipitate, insoluble in alkalies and acetic acid, soluble in dilute mineral acids.

Zinc salts heated on charcoal in the outer blowpipe flame yield an incrustation, which is yellow when hot, and white when cold, and which, on moistening with cobalt nitrate solution and heating strongly, yields a fine green colour.

Physiological Action.—Emetic and poisonous (see *sulphate and chloride*).

CADMIUM.†

Cd = 112.‡ *Specific gravity*, 8·7. *Melting point*, 320°; *boiling point*, 763° *to* 772°. *Specific heat*, 0·056. *Dyad.*

Occurrence in Nature.—This metal is found in combination only, generally accompanying zinc ores, which frequently contain from 1 to

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* It absorbs, for example, hydrogen sulphide, and ammonia, which are among the offensive gases given off by putrefying organic matters, and acts as an antiseptic, chiefly by virtue of its affinity for water.

† The term *cadmia fornacum* is used by Pliny to denote the sublimate in brassfounders' furnaces; hence, the name of this metal which is found in the sublimate from zinc furnaces.

‡ See p. 59.

3 per cent. of it. It occurs less frequently, as the sulphide in the mineral *greenockite*. It belongs to the rarer class of elements.

Properties.—The metal resembles tin in colour, it is comparatively hard, and is both malleable and ductile; it is volatile at a somewhat low temperature, melting at 320°, and boiling at about 770°. It gradually becomes tarnished in contact with air, and, if strongly heated in presence of air, takes fire and burns to oxide. Cadmium vapour decomposes water vapour at a red heat. Cadium is most easily soluble in nitric acid, less easily in dilute hydrochloric and sulphuric acids. It is precipitated from its solutions by zinc. It forms a number of alloys which are characterised by their low melting point.

Preparation.—Being more volatile than zinc, it comes over with the first portions of zinc vapour in the distillation of that metal (see zinc); it is, therefore, found as oxide mixed with zinc oxide in the condensers of the zinc furnaces. These mixed oxides are again reduced by mixing with coal and heating in the retorts, and the cadmium again distils over first; the metal so obtained may be purified by redistillation, solution in hydrochloric acid, and final precipitation by metallic zinc.

Cadmium Oxide, $Cd\,O = 128$. *Specific gravity*, 6·5 (*water* = 1).

Properties.—Cadmium oxide is brown in colour, it is infusible at a white heat. Heated on charcoal it is temporarily reduced, but the metal burns again to oxide, forming a characteristic brown incrustation on the charcoal.

It forms a hydrate, $Cd\,(H\,O)_2$, which may be obtained as a white flocculent precipitate on addition of caustic potash, soda or ammonia solution to a solution of one of its salts, and which is soluble in excess of the last only.

Preparation.—By heating the hydrate or carbonate, or by burning the metal in air.

Salts of Cadmium.—The normal *carbonate*, $Cd\,C\,O_3$, is not well known; a basic salt is obtained by adding a solution of potassium carbonate to a solution of a cadmium salt. The *nitrate*, $Cd\,(N\,O_3)_2$, $4\,H_2\,O$, is very deliquescent. The *sulphate*, $Cd\,S\,O_4$, $4\,H_2\,O$, is obtained in monoclinic crystals by dissolving the oxide or carbonate in dilute sulphuric acid; it is very soluble in water. The *sulphide*, $Cd\,S$, which, as already mentioned, occurs native, is characterised by a splendid yellow colour, and is used as a pigment; it is precipitated by hydrogen sulphide from a solution of a cadmium salt. The chloride, $Cd\,Cl_2$, $2\,H_2\,O$, is an efflorescent salt; it loses its water at a comparatively low temperature, melts at a red heat, and finally sublimes unchanged.

Distinguishing Characters of Cadmium Salts.—The cadmium salts are colourless unless the acid is coloured. Solutions of cadmium salts give with solutions of the *caustic alkalies* a white precipitate of the hydrate, $Cd(HO)_2$, soluble in excess of ammonia only; with the fixed alkaline carbonates and ammonium carbonate, a white precipitate insoluble in excess; with *hydrogen sulphide* and *alkaline sulphides*, a yellow precipitate (CdS), insoluble in excess of the latter (*cf.* arsenic).

Cadmium salts, when heated in the outer blowpipe flame on charcoal, yield a characteristic brown incrustation (CdO).

Physiological Action.—Emetic and poisonous.

LEAD.*

(*Latin*, *Plumbum*) ***Pb*** = 207 *Specific gravity*, 11·25 *to* 11·45 (*water* = 1).
Specific heat, 0·0314. *Melting point*, 334°.† *Dyad.*

Occurrence in Nature.—Lead is very seldom found native; its chief ore is *galena* or *lead sulphide* (PbS); it is found in smaller quantity as *carbonate* in *cerussite* ($PbCO_3$), and in still smaller quantity in numerous minerals as sulphate, chromate, tungstate, molybdate, phosphate, arsenate, oxychloride, &c., and in combination with some rarer elements such as selenium, tellurium, &c.

The sulphide is usually accompanied by silver.

Properties.—Lead is bluish-white or grey in colour; it is extremely malleable, and is ductile, but its tenacity is but slight; it is a soft metal, being easily cut with a knife; it leaves a mark when rubbed on paper. It melts at a comparatively low temperature (334°); it volatilises partially at a bright red heat, but its boiling point is very high, and it cannot, therefore, be distilled like zinc.

When freshly cut, the metal has a very bright surface, which soon becomes dull in moist air from slight oxidation. Heated to a high temperature in contact with air it burns to monoxide.

Fresh lead surfaces, in contact with aërated water, becomes oxidised with formation of the hydrated monoxide, $Pb(HO)_2$, which is somewhat soluble in water; the corrosive action is increased if ammonium salts are present, but is retarded by sulphates, phosphates, carbonates, and free carbonic anhydride, owing to the formation of insoluble salts; a large excess of carbonic anhydride again increases the solvent action. This action of water on lead is of great practical importance since the dissolved oxide excits a highly poisonous action on the human system. Galvanised iron cisterns are, therefore, generally preferable, but slate cisterns are the best of all for domestic purposes.

Lead decomposes water at a white heat only, with evolution of

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* Anglo-Saxon, *lead.*

† 334° by *mercury thermometer;* 326·2° by *air thermometer* (*Person*).

hydrogen and formation of monoxide of lead; it is scarcely acted upon by dilute acids, except nitric acid, in which it is very soluble; strong hydrochloric acid dissolves it, especially on warming, and strong sulphuric acid also dissolves it, more especially if the metal is pure.

Lead may be obtained in octahedra by allowing the molten metal to solidify partially, and pouring off the liquid portion after a time. It is deposited in a tree-like mass (*lead-tree*), when a piece of zinc is suspended in a solution of the acetate; tin and iron also precipitate it from its solutions.

Commercial lead is generally contaminated with antimony, copper, iron, silver, and sometimes with bismuth, nickel, tin, and zinc.

Lead forms a number of important alloys, among which may be mentioned, *solder* and *pewter* (lead and tin), *type-metal* (lead and antimony), and *shot* (lead and arsenic).

Preparation.—There are three processes by which lead is obtained from its ores:—1. *Air-reduction process.*—This is generally employed when the ore consists of comparatively pure galena; the ore is roasted at a moderate heat in a specially constructed furnace, so that a portion is converted into sulphate or oxide, the mass is then thoroughly mixed, and the oxide and sulphate react on the remaining sulphide as indicated in the following equations, with the production of metallic lead, which is drawn of in the molten state:—

$$2\,PbO + PbS = 3\,Pb + SO_2,$$
$$PbSO_4 + PbS = Pb_2 + 2\,SO_2.$$

2. *Precipitation process.*—This process is less often used, and only when the lead ore contains much silica, and when other metals, such as copper, are present; it consists in heating together iron scrap, and either the unroasted or roasted ore, metallic lead is separated, and a sulphide of iron (containing more or less sulphide of lead) is formed.

3. *Carbon-reduction process.*—In Scotland and the North of England, ignited peat is used in the furnaces, and assists in the reduction of the roasted ore.

OXIDES OF LEAD.

Lead Suboxide, . .	Pb_2O.
Lead Monoxide, . .	PbO.
Lead Sesquioxide, . .	Pb_2O_3.
Triplumbic Tetroxide, .	Pb_3O_4.
Lead Dioxide, . .	PbO_2.

Only the monoxide yields salts.

Lead Suboxide, $Pb_2O = 430$. A velvet-black powder, which, when heated in air, burns to monoxide, or, if heated out of contact with air, splits up into lead monoxide and metallic lead. It may be prepared by heating lead oxalate ($Pb\,C_2\,O_4$) to a temperature of 300°, air being excluded.

Lead Monoxide (*litharge*, *massicot*), $Pb\,O = 223$. *Specific gravity*, 9·36 (*water* = 1).

Occurrence.—This oxide has been found in nature, but is a comparatively rare mineral.

Properties.—A yellow or pale-red, very heavy powder; it fuses at a red heat; it is slightly soluble in water, and the solution has an alkaline reaction; it is also soluble in solution of potassium hydrate, and may be obtained from this solution in anhydrous rose-coloured crystals. It melts at a red heat, and solidifies on cooling to a crystalline mass. It is easily reduced when heated with organic substances, or on charcoal. It combines easily with silica, and hence attacks clay crucibles when melted in them. It is a basic oxide, forming a large series of salts. It forms a hydrate [$Pb\,(H\,O)_2$?], which may be obtained by precipitating a solution of a lead salt with a solution of potassium hydrate.

It is largely used in the arts in the manufacture of lead pigments, of lead plaster, of glass and earthenware, &c.

Preparation.—By the oxidation of metallic lead in a current of air; at a moderate heat a yellow powder *(massicot)* is obtained, at a higher temperature a reddish powder, which if fused yields a crystalline mass (*litharge*).

Lead Sesquioxide, $Pb_2\,O_3 = 462$. [$Pb\,O\,.\,Pb\,O_2$].

This a reddish-yellow powder of somewhat doubtful composition, which is precipitated on addition of sodium hypochlorite to a solution of lead monoxide in caustic potash; it appears to be a feeble combination of the monoxide and dioxide, being split up into these two oxides by heating with an acid.

Triplumbic Tetroxide (*red lead*, *minium*), $Pb_3\,O_4 = 685$. [$2\,Pb\,O, Pb\,O_2$]. *Specific gravity*, 8·62 (*water* = 1).

Properties.—This oxide is a brilliant red, very heavy powder; on moderately heating it becomes very dark, but assumes the original colour on cooling; heated above 400° it yields up part of its oxygen, and is converted into monoxide. It appears to be a compound of two molecules of monoxide, with one molecule of dioxide; heated with strong sulphuric acid, it yields oxygen and lead sulphate; with nitric acid, lead nitrate and dioxide; and with hydrochloric acid, lead chloride and chlorine. Red lead is largely used in the arts as a pigment, and in the manufacture of glass.

Preparation.—By long heating of lead monoxide at a gentle red heat in contact with air; the beauty of the colour much depends upon the care expended upon the preparation of the oxide; the commercial product is not a pure tetroxide, but a mixture of this with monoxide, sesquioxide, &c., and it is further much adulterated with ferric oxide, brick dust, &c.

Lead Dioxide (*lead peroxide, brown oxide of lead*), $Pb\ O_2 = 239$. *Specific gravity*, 9·45 (*water* = 1).

Occurrence.—Occasionally found native as *heavy lead ore* in black hexagonal crystals.

Properties.—A dark-brown very heavy powder. On strongly heating it yields up half its oxygen, and is converted into monoxide. Heated with strong sulphuric acid it yields lead sulphate and oxygen; with hydrochloric acid, lead chloride and chlorine; it is unacted on by nitric acid. Dry lead peroxide and dry sulphurous anhydride unite with much evolution of heat to form lead sulphate, when brought into contact with one another, - $Pb\ O_2 + S\ O_2 = Pb\ S\ O_4$. It possesses feeble acid characters; when fused with caustic potash or soda, it forms compounds termed *plumbates* ($K_2\ Pb\ O_3$, $Na_2\ Pb\ O_3$), from which corresponding compounds of other metals may be formed; it resembles manganese dioxide in this respect.

Preparation.—1. By digesting *red lead* ($2\ Pb\ O$, $Pb\ O_2$) with dilute nitric acid; lead nitrate is formed and goes into solution, and the dioxide remains, being insoluble. This is the usual method employed.

2. By mixing a solution of lead acetate, with a solution of sodium carbonate, and passing chlorine through the suspended plumbic carbonate so precipitated; the lead carbonate is completely converted into dioxide with evolution of carbonic anhydride, and simultaneous formation of free acetic acid and sodium chloride. The dioxide may be collected and washed.

3. By heating powdered lead acetate with a solution of bleaching powder to boiling.

SALTS OF LEAD.

Lead Carbonate (*plumbic carbonate, lead spar*), $Pb\ C\ O_3 = 267$. *Specific gravity*, 6·45 (*water* = 1).

Occurrence.—This salt occurs native crystallised in needles or fibrous masses in the mineral *cerussite.*

Properties.—A white very heavy powder; it is very sparingly soluble in water, requiring about 50,000 times its weight for solution; but is more soluble in water containing carbonic anhydride in solution. A basic carbonate is much used as a pigment, and possesses special advantages as such, on account of which, in spite of its poisonous character, and that it is blackened by sulphuretted hydrogen; it has not been superseded by *zinc-white* ($Zn\,O$), or by *baryta-white* ($Ba\,S\,O_4$).

Preparation.—1. By precipitating a solution of a lead salt with a solution of ammonium carbonate. 2. By passing carbonic anhydride into a solution of lead acetate.

Manufacture.—The manufacture of *white lead* is of very ancient date, and is still carried on in Holland and Germany with but little modification; the process, which is of a somewhat complicated nature, consists essentially in exposing rolls of lead plate to the combined action of acetic acid vapour, carbonic anhydride and water at a slightly elevated temperature; the pieces of lead are suspended over acetic acid contained in the bottom of pots, which are then covered first with boards and next with a layer of stable-manure or tan, and a series of such structures are built up.

The first action which ensues is probably the formation of a basic acetate of lead [$Pb\,O, Pb\,(C_2\,H_3\,O_2)_2$], which is in turn decomposed by the carbonic anhydride given off from the decaying and heated manure, with formation of lead carbonate and normal lead acetate, thus:—

$$\overset{\substack{\text{Carbonic}\\\text{Anhydride.}}}{C\,O_2} + \overset{\text{Basic Lead Acetate.}}{Pb\,O, Pb\,(C_2\,H_3\,O_2)_2} = \overset{\substack{\text{Lead}\\\text{Carbonate.}}}{Pb\,C\,O_3} + \overset{\substack{\text{Normal}\\\text{Lead Acetate.}}}{Pb\,(C_2\,H_3\,O_2)_2},$$

The rolls are taken out at suitable times, and the coating of carbonate and acetate removed, and finally washed to remove the acetate.

In this manner a very dense white powder is obtained, which, as already stated, is specially adapted for use as a pigment; it always contains a certain proportion of lead oxide. Lead carbonate produced by precipitation does not appear to constitute an equally suitable material, but much is manufactured by passing carbonic anhydride into a solution of lead acetate.

Lead Nitrate (*plumbic nitrate*), $Pb\,(N\,O_3)_2 = 331$. $[(N\,O_2)_2\,.\,O_2\,Pb]$.

Properties.—This salt crystallises in regular, anhydrous octahedra isomorphous with barium and strontium nitrates; it is soluble in about 7·5 times its weight of water, less soluble in dilute nitric acid, and nearly insoluble in strong nitric acid. On heating strongly it is decomposed into lead monoxide, oxygen, and nitric peroxide (*q.v.*, p. 126). When its solution is heated with lead monoxide a basic nitrate is formed.

Preparation.—By dissolving metallic lead, or the monoxide or the carbonate of lead, in dilute nitric acid, and evaporating to crystallisation.

Lead Sulphate (*plumbic sulphate*), $Pb\,S\,O_4 = 303$. $[S\,O_2\ .\ O_2\,Pb]$. *Specific gravity*, 6·2 (*water* = 1).

Occurrence.—This salt occurs native in *anglesite*, and is isomorphous with barium and strontium sulphates.

Properties.—A white heavy powder soluble in about 22,000 times its weight of water.

Preparation.—By precipitating a solution of a lead salt with sulphuric acid or a soluble sulphate.

Lead Sulphide, $Pb\,S = 239$. *Specific gravity*, 7 *to* 7·6 (*water* = 1).

Occurrence.—As *galena*, a common ore of lead.

Properties.—The native sulphide crystallises in the cubic system, and has the appearance of metallic lead; it is soluble in hydrochloric acid on boiling, with evolution of hydrogen sulphide; nitric acid partly converts it into sulphate, partly into nitrate.

The sulphide produced artificially by precipitating a solution of a lead salt with hydrogen sulphide is a black amorphous powder. Heated in an atmosphere of hydrogen or carbonic anhydride, it may be sublimed at a red heat, the sublimate being highly crystalline. Other sulphides, viz., $Pb_4\,S$ and $Pb_2\,S$, are known.

Preparation.—1. By precipitating a solution of a lead salt with hydrogen sulphide. 2. By passing sulphur vapour over metallic lead.

Lead Chloride, $Pb\,Cl_2 = 278$. *Specific gravity*, 5·80 (*water* = 1). *Melting point*, 498°.

Properties.—This salt crystallises in fine rhombic needles; it is difficultly soluble in water, requiring 135 times its weight of water at 12·5°, but only 30 times its weight of boiling water; it is more difficultly soluble in dilute hydrochloric acid, but more easily soluble in the strong acid.

Preparation.—1. By precipitation from a concentrated solution of a lead salt with hydrochloric acid. 2. By acting on oxide or carbonate of lead with strong hydrochloric acid.

Lead Oxychlorides.—A number of *oxychlorides* are known, some of which are of value as pigments, *e.g.*, *Pattinson's white oxychloride* ($Pb\,Cl_2$, $Pb\,O$, $H_2\,O$), *Turner's patent yellow* ($Pb\,Cl_2$, $7\,Pb\,O$); they are obtained under various conditions, such as the precipitation of a solution of lead chloride with ammonia, fusion of lead chloride and oxide, &c.

General Characters of Lead Salts.—With the exception of the nitrate and acetate, lead salts are difficultly soluble in water. They are mostly colourless; the chromate and iodide are yellow; the precipitated sulphide is black.

Solutions of lead salts yield with solutions of *caustic alkalies* a white precipitate of hydroxide, $Pb(HO)_2$, soluble in excess of the precipitant; with *alkaline carbonates*, a white precipitate, $PbCO_3$; with *potassium chromate*, a pale-yellow precipitate, $PbCrO_4$; with *potassium iodide*, a yellow precipitate, PbI_2; with *dilute sulphuric acid*, a white precipitate; with *hydrochloric acid*, a white precipitate, $PbCl_2$, soluble in much hot water, the solution yields crystalline needles on cooling. This last is a very characteristic test.

Hydrogen sulphide or *ammonium sulphide* produces in solutions of lead salts a black precipitate; a red precipitate is sometimes produced by hydrogen sulphide, in the presence of much hydrochloric acid, and consists of lead chlorosulphide, $PbCl_2, 3PbS$.

The *white* precipitate with sulphuric acid, and the *black* precipitate with hydrogen sulphide, are, taken together, specially characteristic of lead; no other metal yielding these two reactions.

Lead salts heated on charcoal yield a white, very malleable globule, and a yellow incrustation of oxide; the globule marks paper.

Physiological Action.—Lead salts possess a metallic taste and are poisonous, and very apt to produce chronic poisoning by the cumulative action of small doses.

THALLIUM.*

Tl = 203·6. *Specific gravity*, 11·9 (*water* = 1). *Specific heat*, 0·0336.

Occurrence in Nature.—This metal occurs in minute quantities in certain iron and copper pyrites, and was first observed in the flue dust of a sulphuric acid manufactory by Crookes in 1861. It has since then been shown to be contained in a mineral called *crookesite*, found in Sweden; it is also present in a few mineral waters.

Properties.—Thallium is a white metal, a good deal softer than lead, and, like that metal, leaving a mark when rubbed on paper; it melts at 290°, and may be volatilised at a higher temperature; it oxidises somewhat rapidly in contact with air, but may be kept unaltered under water; it is easily soluble in nitric or sulphuric acid.

Preparation.—The flue dust is treated with dilute sulphuric acid, and from this solution, after removal of the commoner metals, the thallium may be obtained by various methods, such as precipitating thallous chloride by addition of hydrochloric acid, redissolving the precipitate in sulphuric acid, and precipitating the metal with zinc, or by precipitating the iodide, &c.

Oxides and Salts.—Thallium forms two oxides, a monoxide, TlO, and a trioxide, Tl_2O_3. The monoxide forms a hydrate which is specially characterised by being easily soluble in water, forming an alkaline solution, which absorbs carbonic anhydride. Both oxides are basic, and form salts, of which a very large number have been prepared. Thallous carbonate, Tl_2CO_3, is soluble in water. Thallous chloride, $TlCl$, is precipitated

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* *θαλλος, a young shoot or twig*, in allusion to the green line of its spectrum

from solutions of thallous salts by dilute hydrochloric acid, or by a solution of a soluble chloride.

Distinguishing Tests.—Thallium salts impart a green colour to the flame of a Bunsen burner; the colour is absolutely monochromatic, and yields a characteristic spectrum consisting of one bright line in the green.

MANGANESE.*

Mn = 55. *Specific gravity*, 7 *to* 8 (*water* = 1). *Specific heat*, 0·1217.
Melts at a white heat. Dyad to Hexad.

Occurrence in Nature.—Manganese is a very widely diffused element, occurring chiefly in traces, and often accompanying iron as a constituent in numerous minerals, in plants, and in the animal body.

It occurs more rarely in large deposits and chiefly as *oxide*, most commonly as dioxide ($Mn O_2$) in the minerals *pyrolusite* (a very pure form), and in *wad* and *psilomelan* (less pure forms); it further occurs as *braunite* ($Mn_2 O_3$), *manganite* ($Mn_2 O_3$, $H_2 O$), *hausmannite* ($Mn_3 O_4$), and as *carbonate* in *manganese spar* ($Mn C O_3$). It is also found as sulphide.

Properties.—Manganese is a greyish metal with a tinge of red, very hard and brittle, scratching glass; it oxidises rapidly in moist air, and has therefore to be kept out of contact with air, generally under naphtha. It is feebly magnetic. When in a fine state of division, it decomposes water at moderate temperatures; it is readily soluble in acids. It is not used by itself, but is occasionally alloyed with other metals, such as steel. Some of its compounds are, however, used extensively.

Preparation.—1. The oxide obtained by heating manganous carbonate, is mixed with one-tenth of its weight each of charcoal and borax, and heated in a blast furnace to a white heat in a covered and luted crucible. 2. By heating manganous chloride or fluoride with sodium. 3. By the electrolysis of an aqueous solution of manganous chloride.

OXIDES OF MANGANESE.

Manganese yields a very complete series of oxides, comprising all varieties; basic, neutral, and acid-forming.

Manganous Oxide, . .	$Mn O$.
Manganic Oxide, . .	$Mn_2 O_3$.
Trimanganic Tetroxide, .	$Mn_3 O_4$.
Manganic Peroxide, . .	$Mn O_2$
Manganic Anhydride (?), .	$Mn O_3$.
Permanganic Anhydride, .	$Mn_2 O_7$.

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* For derivation of *manganese* see *magnesium*, p. 237.

Manganous Oxide (*protoxide of manganese, manganese monoxide*), $Mn\,O = 71$. *Specific gravity, of native*, 5·18; *of artificial*, 4·72 *to* 5·09.

Occurrence.—As the mineral *manganosite.*

Properties.—This oxide may be obtained as a pale or dark-green amorphous powder, or in emerald-green transparent regular octahedra, according to its method of preparation. Prepared at a low temperature it soon becomes converted into red oxide ($Mn_3\,O_4$), even at ordinary temperatures and when gently heated oxidises rapidly, becoming red hot in the process. Prepared at high temperatures it is permanent in air at ordinary temperatures, but oxidises rapidly when strongly heated. It is a powerfully basic oxide, yielding salts, which for the most part are of a delicate pink colour, isomorphous with ferrous salts. When pure it dissolves in hydrochloric acid without the evolution of chlorine; it is readily soluble in chloride of ammonium solution, with evolution of ammonia. It cannot be reduced to the metallic state by heating in hydrogen.

Preparation.—*Amorphous*, by heating manganous carbonate with exclusion of air; by heating any oxide of manganese in a carbon crucible for some time to a white heat. *Crystalline*, by heating the amorphous oxide in a current of hydrogen, mixed with a small proportion of hydrochloric acid gas.

Manganous Hydrate (*hydrated manganous oxide; manganous hydroxide*), $Mn\,H_2\,O_2 = 89$. $[Mn\,O, H_2\,O]$.

Occurrence.—As the mineral *pyrochroit.*

Properties.—A white flocculent precipitate, becoming brown on exposure to air, rapidly oxidising, chiefly to hydrated sesquioxide ($Mn_2\,O_3$, $H_2\,O$), when free from alkali, but in presence of an alkali to hydrated peroxide ($Mn\,O_2$, $H_2\,O$). It is readily soluble in acids. Heated in a current of hydrogen it yields manganous oxide. It is soluble in a solution of manganous chloride, imparting to it an alkaline reaction.

Preparation.—By precipitating a solution of a manganous salt by sodium or potassium hydroxide, with exclusion of air. Any oxide of manganese when boiled for some time with strong hydrochloric acid yields a solution of manganous chloride, from which caustic alkalies precipitate manganous hydrate.

Manganic Oxide (*manganese sesquioxide*), $Mn_2\,O_3 = 158$.

Occurrence.—As the mineral *braunite.*

Properties.—The native *braunite* is found in brownish-black crystals belonging to the square prismatic system, of semi-metallic lustre, and of specific gravity 4·75 to 4·82. Artificially prepared it is a black, or when very finely divided, a brown powder of specific gravity 4·325. Heated to redness in air, it loses 3 to 3·5 per cent. of oxygen, and yields $Mn_3 O_4$; heated in a current of hydrogen it yields $Mn O$. When boiled with nitric acid it yields a solution of manganese nitrate and insoluble peroxide; it dissolves in strong boiling sulphuric acid with evolution of oxygen and formation of manganous sulphate. Boiled with strong hydrochloric acid it yields chlorine and manganous chloride.

Preparation.—1. By heating any oxide of manganese in oxygen. 2. By careful heating of manganic hydrate.

Manganic Hydrate, $Mn_2 H_2 O_4 = 176$. $[Mn_2 O_3, H_2 O]$.

Occurrence.—As the mineral *manganite.*

Properties.—*Native* manganic hydrate is found in dark steel-grey opaque crystals of the right prismatic system, having a specific gravity of 4·22, and of imperfect metallic lustre. Artificially prepared, it is a reddish-brown powder, which, when dried at 100°, contains one molecule of water. When quite pure it is insoluble in dilute sulphuric acid, but readily soluble in the presence of manganous oxide. Heated with concentrated sulphuric acid at a temperature a little above 100°, it becomes converted into a green mass of manganic sulphate, no oxygen being evolved. Heated to redness in air it loses water, and yields $Mn_3 O_4$.

Preparation.—By decomposing the sulphate with much water, and washing the resulting hydrated oxide.

Mangano-Manganic Oxide (*red oxide of manganese; trimanganic tetroxide*), $Mn_3 O_4 = 224$. $[Mn O, Mn_2 O_3]$.

Occurrence.—As the mineral *hausmannite.*

Properties.—The native oxide occurs in square prismatic crystals, which are opaque, and of imperfect metallic lustre, and of a brownish-black colour; specific gravity, 4·7 to 4·8. Artificially prepared, it is a brownish-red powder, and black when hot; specific gravity, 4·3 to 4·7. It is reduced to manganous oxide ($Mn O$) by heating in a current of hydrogen; it is converted into manganic oxide ($Mn_2 O_3$) by heating in oxygen. Boiled with solution of chloride of ammonium, manganous oxide goes into solution while manganic oxide remains behind. It is soluble in small quantity in hot concentrated phosphoric acid, and in cold sulphuric, hydrochloric, oxalic, or tartaric acids, without neutralising the acids. Addition of water or heating converts these solutions, with the exception of the phosphoric acid, into solutions of manganous salts. It forms a chocolate-brown hydrate of uncertain composition.

Preparation.—By spontaneous oxidation of an ammoniacal solution of manganous oxide, containing chloride of ammonium.

Manganic Peroxide (*peroxide of manganese, black oxide of manganese, manganese dioxide*), $Mn\,O_2 = 87$.

Occurrence.—As the mineral *pyrolusite*, crystallised; compact, earthy or pseudomorphous after *calcite*, *manganite*, or *polianite* in veins and beds in various rocks, and as a deposit in the deep oceans—as *polianite*.

Properties.—Pyrolusite is found in crystals belonging to the right prismatic system, dark grey to black, of metallic lustre, and of specific gravity 4·70 to 5·0. Polianite also crystallises in the right prismatic system, but in different forms; it is of a light steel-grey colour, opaque, of feeble metallic lustre, and of specific gravity 4·838 to 4·880. Artificially prepared, it is a black crystalline powder. Heated to redness, peroxide of manganese is reduced to the red oxide ($Mn_3\,O_4$); heated to redness in hydrogen it yields manganous oxide ($Mn\,O$), in oxygen manganic oxide ($Mn_2\,O_3$). It is soluble in cold concentrated hydrochloric acid with evolution of chlorine.

Acted on by strong sulphuric acid it yields at 110° manganic sulphate, losing thereby a quarter of its oxygen; heated more strongly it yields manganous sulphate, and loses another quarter of its oxygen. It is readily soluble in dilute sulphuric acid, containing potassium iodide in solution, with liberation of iodine. It is a powerful oxidising agent in presence of sulphuric acid.* It acts as a feeble acid in presence of strong alkalies.

Uses.—Chiefly for the manufacture of chlorine (p. 169), of manganates and permanganates, for decolorising glass containing iron, and for imparting to glass a purple colour.

Preparation, &c.—By very carefully heating manganous nitrate with two parts of potassium chlorate to 300°, and washing the residue with water. The native oxide is sufficiently pure for manufacturing purposes.

Hydrated Manganese Peroxide, $Mn\,H_2\,O_3 = 105$. $[Mn\,O_2,\,H_2\,O]$.

Preparation.—By boiling any of the oxides of manganese lower than the peroxide with concentrated nitric acid. By precipitating a manganous salt by means of a hypochlorite.

Properties.—Brownish-black or black powder; reddens litmus. Expels carbonic anhydride from solutions of alkaline carbonates, as well as from precipitated carbonates of calcium and barium. Loses water in air dried by sulphuric acid, but very gradually only; does

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* Oxalic acid is oxidised by it in the presence of diluted sulphuric acid to carbonic anhydride, $Mn\,O_2 + H_2\,S\,O_4 + C_2\,H_2\,O_4 = Mn\,S\,O_4 + 2\,C\,O_2 + H_2\,O$. The amount of carbonic anhydride evolved is a measure of the proportion of peroxide contained in the sample experimented with

not become anhydrous at 210°, but begins to lose oxygen at that temperature. It possesses acid properties, and forms compounds termed *manganites* (p. 270).

Weldon's Process.—Air blown into water holding manganous hydrate in suspension oxidises the same to manganic hydrate, but in the presence of a basic oxide oxidation goes further, and the manganous hydrate is oxidised to manganese peroxide, which combines with the basic oxide yielding a manganite. Weldon's process for the regeneration of manganese is based on this reaction. The solution of manganous chloride remaining after the preparation of chlorine (p. 170), is mixed with milk of lime, and air and steam is blown through the mixture; at a temperature of from 55° to 75° oxidation takes place rapidly, and about 79 per cent. of the manganese may in this way be obtained in the form of peroxide, combined partly with lime, partly with manganous oxide. The reaction may be represented as follows:—

$$124\,Mn\,Cl_2 + 160\,Ca\,H_2O_2 + 98\,O = 124\,Ca\,Cl_2 + 36\,(Ca\,O, 2\,Mn\,O_2) + 26\,(Mn\,O, Mn\,O_2) + 160\,H_2O.$$

The precipitate is allowed to subside, the clear supernatant fluid run off, and hydrochloric acid added to the precipitate, chlorine, manganous chloride, and chloride of calcium are again produced; the manganous chloride once more precipitated by milk of lime, air and steam are blown through, &c.

SALTS OF MANGANESE.

Manganous oxide is a powerful base, and yields salts isomorphous with the corresponding ferrous salts, in which the manganese is a dyad; they are either pink or white.

Manganous Carbonate, $Mn\,C\,O_3 = 115$, occurs native as *manganese spar* (specific gravity, 3·6), and may be obtained as a white precipitate on adding a solution of an alkaline carbonate to a solution of a manganous salt.

Manganous Nitrate, $Mn\,(N\,O_3)_2, 6\,H_2\,O = 179 + 108 = 287$. *Specific gravity*, 1·8 (*water* = 1). *Melting point*, 25·8.

Prepared by dissolving the carbonate in nitric acid; it crystallises in white deliquescent needles, and is easily decomposed by heat.

Manganous Sulphate, $Mn\,S\,O_4, 7\,H_2\,O = 151 + 126 = 277$.

At temperatures below 6° this salt crystallises with 7 molecules of water and is isomorphous with ferrous sulphate ($Fe\,S\,O_4$, $7\,H_2\,O$), while at temperatures between 7° and 20° it crystallises with 5 molecules of water, and is isomorphous with sulphate of copper ($Cu\,S\,O_4$, $5\,H_2\,O$). At a temperature of 200° the salt becomes anhydrous. It forms double sulphates with the alkalies. It is easily soluble in water and somewhat less soluble at higher temperatures.

Preparation.—By heating peroxide of manganese with strong sulphuric acid, extracting the mass with water, digesting the solution with manganous carbonate to precipitate the iron, and crystallising.

Manganous Chloride, $Mn\ Cl_2 = 126$.

This salt is obtained in solution by heating any of the oxides of manganese with hydrochloric acid. It crystallises in pink or white crystals with 4 molecules of water, which are extremely soluble in water; the solubility does not increase above 62·5°. It is deliquescent.

Manganous Phosphates.—A great variety of phosphates of this oxide are known, most of which can be obtained in the form of a white precipitate by adding the various sodic phosphates to a solution of a manganous salt.

The precipitates contain various proportions of water according to their method of production, and may be obtained anhydrous by heating to redness.

Manganic Salts.—These salts, in which the manganese is a pseudo-triad, are very unstable, and readily break up into manganous salts and oxygen. *Manganic Sulphate*, $Mn_2\,(S\,O_4)_3$, is obtained by the action of sulphuric acid on hydrated peroxide of manganese. It is a green powder decomposed by water into hydrated sesquioxide of manganese and sulphuric acid.

Dissolved in diluted sulphuric acid, it yields an alum with sulphate of potassium (see p. 246).

Manganites.—Peroxide of manganese yields compounds with basic oxides (see Weldon's process, p. 269), which may be looked upon as salts of a manganous acid, $H_2\,Mn\,O_3$. Several of these compounds are found native, *e.g.*, *psilomelan*, *varvicite*, *wad*, chiefly $Mn\,O$, $Mn\,O_2$ in varying proportion, and generally hydrated; *crednerite*, chiefly $Cu\,O$, $Mn\,O$, $Mn\,O_2$, &c.

These compounds may also be prepared artificially, and one of them, namely, the calcium compound, is of considerable practical importance (see p. 269).

Manganates.—Neither **manganic anhydride,** $Mn\,O_3$, nor **manganic acid,** $H_2\,Mn\,O_4$, are known in the free state, but salts of the acid are well known, in which the acid is di-basic and isomorphous with sulphuric acid.

Potassium Manganate, $K_2\,Mn\,O_4 = 197$.

Properties.—This salt is usually in the form of a deep green amorphous mass which dissolves in a little water, particularly in the presence of excess of alkali, yielding a beautiful deep green solution, which on evaporation in vacuo yields rhombic crystals of the manganate. The solution is instantly decomposed by the addition of an acid with formation of permanganic acid; when simply diluted with much water the colour changes rapidly to pink, and becomes turbid, after which permanganate is in solution, and hydrated peroxide precipitated. The solution acts as a strong oxidising agent, and is rapidly decolourised by reducing agents, and by most kinds of organic matter.

Preparation.—By heating peroxide of manganese with potassic hydrate in the presence of air, or with addition of a nitrate or chlorate.

Sodium Manganate, $Na_2\, Mn\, O_4 = 165$.

Perfectly analogous to the potassium salt, and similarly prepared.

Permanganic Anhydride, $Mn_2\, O_7 = 222$.

Dark reddish-brown or greenish-black oily liquid, which does not solidify at $-20°$, and is heavier than oil of vitriol. Detonates when heated rapidly at 30° or 40°. Explodes in contact with sulphur or phosphorus and many organic substances. Evolves ozonised oxygen even at ordinary temperature. When heated slowly it may be partially volatilised, forming a violet vapour. It absorbs moisture from the atmosphere forming a solution of permanganic acid ($H\, Mn\, O_4$), dissolves in water, when added in small quantity at a time, to avoid heating, with formation of permanganic acid.

Preparation.—By acting on potassium permanganate with sulphuric acid, diluted with $\frac{1}{2}$ molecule of water, and carefully distilling at a temperature not exceeding 70°.

Permanganic Acid, $H\, Mn\, O_4 = 120$. $[H_2\, Mn_2\, O_8;\ Mn_2\, O_7,\ H_2\, O]$.

Properties.—This acid is only known in solution, which is dark carmine red in reflected, dark violet in transmitted light, in dilute solution bluish-red. The solution shows five absorption bands. It has very great tinctorial power. It is a powerful oxidising agent, and is readily acted on by reducing agents, or in contact with almost all kinds of organic matter.

Preparation and Formation.—By dissolving permanganic anhydride in cold water. By precipitating a solution of barium permanganate with the exact proportion of sulphuric acid. By boiling any soluble manganese compound with nitric acid and excess of binoxide of lead.

Potassium Permanganate, $K\, Mn\, O_4 = 158$. $[K_2\, Mn_2\, O_8]$.

Properties.—Rhombic prisms of deep red colour by transmitted light, almost black and metallic looking by reflected light. Soluble in 16 parts of water at ordinary temperature, but in less at higher temperatures.

The solution is a powerful oxidising agent, deodorant and disinfectant, and is readily decomposed in presence of almost all kinds of organic matter.

Preparation.—By boiling a solution of potassium manganate (if alkaline, carbonic anhydride should be passed in during the boiling), filtering from the hydrated peroxide thrown down, through asbestos or through glass wool (contact with all kinds of organic filtering materials has to be avoided), and evaporating to crystallisation. The salt is isomorphous with potassium perchlorate, and hence cannot be purified from this salt by crystallisation.

Sodium Permanganate, $Na\,Mn\,O_4 = 142$. $[Na_2\,Mn_2\,O_8]$.

Analogous to, and prepared like, the potassium salt.

Barium Permanganate $Ba\,(Mn\,O_4)_2 = 375$. $[Ba\,Mn_2\,O_8]$.

This is prepared by passing carbonic anhydride into water in which barium manganate is suspended, and evaporating the red solution obtained.

Manganous Sulphide, $Mn\,S = 87$.

Occurs native as *manganese blende* (specific gravity, 4·0); obtained as a greenish powder by heating any oxide of manganese in a current of sulphuretted hydrogen. The hydrated sulphide, $Mn\,S,\ H_2\,O$, is obtained as a flesh-coloured precipitate, when an alkaline sulphide or sulphide of ammonium are added to a solution of a manganous salt; the precipitate is readily soluble in acids.

General Characters and Tests of Manganese Compounds.—All manganese compounds, when fused with carbonate of soda and nitre, yield a green mass of manganate; they impart to a borax bead an amethyst colour in the oxidising flame, but leave it colourless in the reducing flame; when boiled with nitric acid and peroxide of lead they yield a red solution containing permanganic acid.

Manganous salts are pink or white, and their solutions yield a white precipitate ($Mn\,O,\ H_2\,O$), with caustic alkalies speedily becoming brown, a white precipitate ($Mn\,C\,O_3$) with alkaline carbonates, and a flesh-coloured precipitate ($Mn\,S,\ H_2\,O$) with sulphide of ammonium. They are not precipitated by ammonia in presence of chloride of ammonium. When pure they yield no chlorine on heating with strong hydrochloric acid.

All other manganese compounds when boiled with hydrochloric acid yield chlorine, the amount of which is proportional to the amount of oxygen, in excess of that necessary to form manganous oxide present in the compound.

All the oxides when heated for some time to redness in air yield red oxide, $Mn_3\,O_4$.

Physiological Action.—Potassium permanganate is chiefly used externally, but also for injections, as an antiseptic and deodorant.

IRON.*

Fe = 56. *Specific gravity*, 7·8 (*water* = 1). *Specific heat*, 0·1138.
Melting point, from 1000° *to* 2000°. *Dyad to hexad.*

Occurrence in Nature.—Iron is found native in detached masses (meteoric iron), varying from a few grains to many thousand pounds in weight; these masses have fallen from interplanetary space; they contain in addition to iron, which is their main constituent, generally nickel, sometimes in considerable quantity, and varying amounts of cobalt and some other metals, together with sulphide of iron. Native iron of terrestrial origin is but rarely found.

Iron is one of the most abundant, and emphatically one of the most universally diffused of the elements; it is chiefly found as *oxide*, *carbonate*, and *sulphide;* in addition to considerable deposits in these forms it is found in almost all rocks and soils, in spring-water, river-water, and sea-water, in plants, and in the animal body, forming 0·24 per cent. of the colouring-matter of the blood.

The following are its chief ores:—*Specular iron ore* or *red hæmatite* ($Fe_2 O_3$); *brown hæmatite* or *limonite* ($2 Fe_2 O_3, 3 H_2 O$); *magnetic iron ore*, *magnetite*, or *loadstone* ($Fe_3 O_4$); *spathic iron ore* ($Fe C O_3$), and *clay ironstone*, an ore consisting of ferrous carbonate largely mixed with clay; this last is the most important of English iron ores, it is sometimes found mixed with coal, when it is called *black band.*

Iron is also found in great quantities as disulphide in *iron pyrites* ($Fe S_2$), less frequently as *magnetic pyrites* ($Fe_7 S_8$); as sulphide, iron is a constituent of *copper pyrites* ($Cu Fe S_2$), of *arsenical pyrites*, or *mispickel* ($Fe As S$), &c.

Iron occurs further in many other minerals, too numerous to mention, as sulphate, borate, phosphate, silicate, &c., and in combination with chromium in *chrome iron ore* ($Fe Cr_2 O_4$).

Properties.—Pure iron may be obtained crystallised in regular octahedra; it is nearly silver-white, and admits of a very high polish; it may also be obtained in the form of a black amorphous powder, in which form, and when prepared at a low temperature, it is spontaneously inflammable when brought into contact with air. Iron is very malleable and extremely ductile. It oxidises in moist air, forming hydrated sesquioxide ($Fe_2 O_3, 3 H_2 O$), or at higher temperatures

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* Anglo-Saxon, *iren*, *isen;* German, *eisen*, and similar forms in Dutch, Islandic, Danish, Swedish, Welsh, Irish, &c. Skeat says:—"The Teutonic forms exactly correspond to an adjective form from *ice;* perhaps *iron* was named from its smooth hard surface when brightened."

magnetic oxide (Fe_3O_4). It decomposes water at elevated temperatures, and dissolves at ordinary temperatures in dilute mineral acids with evolution of hydrogen; very slowly when perfectly pure. It is not acted on by strong nitric acid. It is fusible only at the highest temperatures.

Pure iron is not used as such in the arts, but is always mixed or combined with varying but small quantities of carbon and some other substances. These admixtures and the various methods of their preparation give rise to several varieties of the metal possessing the most diversified properties and of the highest practical importance. We may, most conveniently, consider the properties of each of these varieties separately, and will refer to their preparation later on.

The action of acids on the three following varieties of iron is essentially the same. Dilute acids dissolve the iron and leave the carbon, which was in combination with the iron in the form of a carbide of iron, Fe_4C, while the rest of the carbon in the form of graphite remains behind. Stronger acids dissolve the iron, and act also on the combined carbon, which is given off in the form of carburetted hydrogen, leaving graphite undissolved. Strong nitric acid has no action on any variety.

Wrought Iron.—This form of iron contains from 0·15 to 0·5 per cent. of carbon. It is of a grey colour, and is capable of a high polish; when containing not more than 0·3 per cent. of carbon, it has a fibrous structure; it can be rolled and hammered. It melts at about 1500° to 2000°, and has the highest melting point of all the varieties of iron. It becomes strongly magnetic under the influence of a galvanic current or in contact with a magnet, but loses its magnetism when such influence is removed, the more completely the softer it is. It is extremely malleable and ductile, and one of the most tenacious of metals. When heated it becomes soft, and may be *welded*, that is, two pieces may be kneaded into one homogeneous piece.

Steel contains usually from 0·6 to 2 per cent. of carbon, but certain forms of mild steel and Bessemer steel contain as little as 0·4 per cent., and greatly resemble wrought iron. It is of grey colour, and can be forged and welded like wrought iron, and fuses at a somewhat lower temperature (about 1300° to 1400°). When heated to a high temperature and suddenly cooled, it becomes extremely hard and brittle, but remains comparatively soft when cooled slowly. Its most characteristic property is that it is capable of being tempered, that is, when hardened steel is again raised in temperature and slowly cooled, it becomes less brittle and softer, and may be obtained highly elastic. The higher the temperature to which it is thus raised the softer it becomes; the temperatures usually employed are between 200° and 300°. In hardened steel the whole of the carbon is in combination with the iron, probably as a definite carbide; in tempered or soft steel, part is in the form of graphite. Hardened steel becomes magnetic only slowly, but retains its magnetism even after the magnetising influence is removed; soft steel losses its magnetism more or less completely after removal of the magnetising influence.

Cast Iron contains from 2 tò 6 per cent. of carbon. When cooled quickly from the molten state, all the carbon remains in chemical combination, the iron is white and extremely hard and brittle. When, on the other hand, the cooling takes place slowly more or less of the carbon crystallises out in the form of graphite, in consequence of which the iron has a grey colour. Cast iron is neither ductile nor malleable and cannot be welded, but breaks readily under a blow, and passes from the solid to the liquid condition without passing through a stage of softness like wrought iron or steel. Ordinary cast iron becomes magnetic, and retains part of the magnetism for some time after the magnetising influence is removed, but cast iron which has been cooled very slowly losses its magnetism almost instantaneously. Its specific gravity is from 7 to 7·25. It melts at about 1050°. The presence of various other substances, more particularly of manganese, prevents the separation of carbon, as, for example, in the variety of iron known as *Spiegeleisen*, from which no carbon crystallises out even during the slowest cooling.

Preparation and Manufacture of the various forms of Iron—*Pure Iron.*—Absolutely pure iron is exceedingly difficult to prepare, and can only be obtained by the strictest attention to the absolute purity of all the materials used. (a) *Crystalline*—By reducing ferrous chloride in a current of hydrogen at an elevated temperature. (b) *In powder*—By reducing ferric oxide in a current of hydrogen at a low red heat (*ferrum redactum*), or by heating pure oxalate of iron in a current of hydrogen.

Wrought Iron.—By heating cast iron with powdered hæmatite (Fe_2O_3), or by heating first in a current of air, stirring in the oxide formed on the surface, and finally heating out of contact with air. During this process, known as the *puddling process*, the iron is stirred with iron rods, and as the carbon is burnt out, it becomes less and less liquid and more tenacious, so that at last it is converted into a soft mass, which is rolled about on the hearth of the furnace in the form of a ball (or *bloom*), which is finally placed under a hammer, press, or roller.

During this process most of the carbon and portions of phosphorus, silicon, and sulphur are removed by oxidation.

Steel.—By heating bars of wrought iron in contact with carbon to a bright red heat, whereby the iron takes up carbon, and hammering or rolling into a homogeneous mass at a bright red heat (*cement steel*), or by subsequent melting (*cast steel*).

By *Bessemer's process*, cast iron is melted and air blown through the mass in specially arranged vessels called *converters;* the carbon is thus burnt, and can be reduced to an extremely low proportion, when it is brought to the desired amount by the addition of Spiegeleisen of known composition. Sulphur, and more particularly phosphorus, cannot thus be removed, but the latter may in great measure be removed by lining the converters with lime.

Cast Iron.—The iron ore, chiefly red and brown hæmatite, clay-iron ore, an impure ferrous carbonate, black band, a ferrous carbonate containing bituminous matter, &c., are frequently first submitted to a process of roasting, whereby they are converted into ferric oxide, and much of the sulphur they contain is burnt off in the form of sulphurous anhydride. The roasted ore is reduced in gigantic furnaces, often 80 feet high and 26 feet internal diameter, called *blast furnaces.* Into these furnaces the roasted ore is introduced in alternate layers with coal and limestone, and, if necessary, silica for the formation of *slag;* usually there is enough silica in the ore itself. Air is forced in at the bottom of the furnace at a temperature of about that of melting lead (*hot blast*).

The coal is burnt to carbonic anhydride (CO_2), which gas, as it passes up through the hot layers of coal above, is reduced to carbonic oxide (CO), and this in its turn reduces the ferric oxide to the metallic condition, being at the same time reconverted into carbonic anhydride; as such, it is once more reduced by contact with a higher layer of red hot coal, and once more becomes carbonic oxide and capable of reducing more ferric oxide. This alternate reduction to carbonic oxide and re-oxidation to carbonic anhydride goes on until the upper and less heated portions of the furnace are reached, and finally a mixture of carbonic oxide and carbonic anhydride escapes at the top of the furnace where the carbonic oxide takes fire. Formerly the carbonic oxide was thus allowed to burn to waste, now, however, it is generally utilised to heat the air for the blast and for other purposes. As the coal in the lower layers thus burns off the whole mass inside the furnace sinks down, and as the reduced metal reaches the hottest part of the furnace it melts and collects at the bottom of the furnace, where it is protected by the fusible slag produced from the lime and silica. In its passage through the hottest part of the furnace the iron takes up chiefly carbon, but also sulphur, phosphorus, silicon and other impurities.

At certain intervals the iron is drawn off from the furnace and run into moulds formed in sand by the side of the furnace, called pigs ; the slag runs off continually.

OXIDES OF IRON.

Ferrous Oxide, . .	$Fe\,O$.
Ferric Oxide, . .	$Fe_2\,O_3$.
Ferroso-ferric Oxide, .	$Fe_3\,O_4$.
Ferric Anhydride, . .	$Fe\,O_3$ (?).

Ferrous Oxide (*protoxide of iron*), $Fe\,O = 72$.

Properties.—A black powder spontaneously inflammable in contact with air, yielding ferric oxide ($Fe_2\,O_3$).

Preparation.—1. By reducing ferric oxide by means of hydrogen at a temperature of from 280° to 300°. 2. By gradually adding ferrous oxalate to a boiling solution of potassium hydrate.

Ferrous Hydrate (*hydrated protoxide of iron*), $Fe\,H_2\,O_2 = 90$. [$Fe\,O$, $H_2\,O$].

Properties.—A white precipitate, having a most powerful affinity for oxygen, so that unless contact with oxygen is absolutely avoided, it speedily turns green, and finally brown, becoming converted into ferric hydrate ($Fe_2\,O_3 \,.\, 3\,H_2\,O$). It is soluble in 150,000 parts of water, yielding a distinctly alkaline solution. It is readily soluble in acids, forming *ferrous* salts, in which the iron is bivalent. It absorbs carbonic anhydride with avidity, and with considerable elevation of temperature.

Preparation.—By precipitating a solution of pure ferrous sulphate with ammonia, under absolute exclusion of oxygen.

Ferric Oxide (*sesquioxide of iron*), $Fe_2\,O_3 = 160$. *Specific gravity*, 4·3 *to* 5·33.

Occurrence.—Found native; massive as red hæmatite, crystallised as specular iron ore ; in combination very widely diffused (see *Iron*).

Properties.—The artificially prepared oxide forms a dark-red powder insoluble in water*. When prepared at a low temperature it is readily

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* A solution of ferric oxide in water may be obtained by dissolving ferric hydrate in ferric chloride, and submitting the solution to dialysis. Ferric chloride passes through the dialyser, leaving ferric oxide, dissolved in water, in the dialyser. The solution is very unstable, and readily breaks up into ferric hydrate and water. A solution of this fluid containing, however, more or less ferric chloride, is known as *dialysed iron*.

soluble in acids, but when strongly heated it becomes almost insoluble in acids; it is again rendered soluble by fusion with alkaline carbonates. It is a feeble basic oxide, forming salts called *ferric* salts, containing two triad atoms of iron in their molecule, the double atom being sexvalent.

Preparation.—By heating ferric hydrate; by heating ferrous sulphate to a red heat.

Ferric Hydrates.—Ferric oxide forms several hydrates, some of which are found native, some are prepared artificially; they all when heated lose water, and become converted into anhydrous ferric oxide. The artificial preparations constitute more or less bulky brownish-red flocculent precipitates, yielding yellowish-brown powders on careful drying; they are all readily soluble in acids. The hydrate, $Fe_2 H_6 O_6$ ($Fe_2 O_3 3 H_2 O$), produced by precipitating a ferric salt with ammonia, may be dried at ordinary temperature, forming a yellowish-brown powder. Dried in vacuo it loses half its water, and has the composition, $Fe_4 H_6 O_9$ ($2 Fe_2 O_3$, $3 H_2 O$); it slowly undergoes a similar change at ordinary temperatures, even when under water. This hydrate is found native as *brown hæmatite*, and constitutes ordinary *iron rust*. When dried at 100° the normal hydrate loses two-thirds of its water, and has the composition, $Fe_2 H_2 O_4$ ($Fe_2 O_3$, $H_2 O$). Dried at 350° it loses all its water, but still remains readily soluble in acids, but when carefully heated to a somewhat higher temperature the oxide begins to glow, and after this glow has proceeded through the entire mass the resulting oxide is soluble in acids with difficulty only.

Preparation.—By precipitating a solution of a ferric salt with ammonia. By precipitating a solution of ferrous sulphate with carbonate of soda, collecting and washing the precipitate, and drying it by exposure to air. (See above.)

Ferroso-Ferric Oxide (*magnetic oxide, black oxide of iron*), $Fe_3 O_4 = 232$. [$Fe O, Fe_2 O_3$].

Occurrence.—Found native as *magnetite*, forming the natural *loadstone; specific gravity*, 4·96 *to* 5·20.

Properties.—The native variety is either massive or crystallised in various forms of the regular system; it is brittle, of more or less metallic lustre, magnetic, and fusible before the blowpipe; it is soluble in warm hydrochloric acid, yielding a mixture of ferrous and ferric salts. It may be artificially produced in black metallic-looking scales, or as a black magnetic powder.

Preparation.—1. By heating iron to bright redness in contact with air. 2. By heating iron to redness in a current of steam (see p. 100).

3. By heating ferrous carbonate (*spathose iron ore*) out of contact with air. 4. By heating the hydrated oxide.

Ferroso-Ferric Hydrate (*hydrated magnetic oxide*), $Fe_3 O_4, H_2 O = 250$. A black magnetic powder, soluble in acids. Heated to 90° it loses its water, and when more strongly heated in contact with air it is converted into ferric oxide.

Preparation.—1. By precipitating a mixed solution of a ferrous and ferric salt in molecular proportions by means of ammonia or potassic hydrate. 2. By precipitating a solution of ferrous sulphate with sodic carbonate, and boiling the washed precipitate in a concentrated solution of potassic hydrate.

Ferric Anhydride (?), $Fe O_3 = 104$.

The existence of this oxide and of its hydrate, $H_2 Fe O_4$, known as *ferric acid*, is assured since salts have been prepared, which correspond to such a hydrate, but neither the oxide nor its hydrate have as yet been prepared. Potassium ferrate ($K_2 Fe O_4$) may be prepared by heating together a mixture of very fine iron filings and nitre, or by passing chlorine through a solution of potassic hydrate, in which ferric hydrate is suspended. It forms dark-red crystals, dissolving in water to a purple solution, which decomposes spontaneously into ferric hydrate, potassic hydrate, and oxygen. Addition of acid decomposes the solution instantaneously, with evolution of oxygen and formation of potassium and ferric salts.

FERROUS SALTS (Fe'').

Ferrous Carbonate, $Fe C O_3 = 116$. *Specific gravity*, 3·7 *to* 3·92.

Occurrence.—Crystallised in the hexagonal system as *spathose iron ore*, generally containing from 2 to 25 per cent. of maganese, and from 0 to 15 per cent. of magnesia, and frequently lime; or mixed with clay and other minerals, in *clay ironstone*, or with bituminous matter, in *black band* iron ore. It is also found dissolved in small quantities in some waters (*chalybeate*[*] *waters*) containing carbonic anhydride in solution; from these it is speedily precipitated in the form of ferric hydrate on exposure to air.

Properties.—Artificially prepared it forms a white powder, which rapidly absorbs oxygen from the air, yielding ferric hydrate and carbonic anhydride. Soluble in water containing carbonic acid (chalybeate springs). Readily soluble in acids.

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[*] Latin, *chalybs*; Greek, χαλυψ, steel, so named from the *Chalybes*, a people of Pontus, on the Black Sea who were great iron-workers.

Preparation.—By precipitating a solution of pure ferrous sulphate with carbonate of soda, with careful exclusion of air, and drying *in vacuo.*

Ferrous Nitrate, $Fe\,(N\,O_3)_2\,6\,H_2\,O = 288$.

This salt is very unstable, and readily absorbs oxygen from the air. It may be prepared by mixing a solution of ferrous sulphate with a solution of barium nitrate, barium sulphate being precipitated.

Ferrous Sulphate (*protosulphate of iron*, *green vitriol*, *copperas*), $Fe\,S\,O_4,\ 7\,H_2\,O = 278$. *Specific gravity*, 1·9.

Occurrence.—In oblique prismatic crystals, as *melanterite*, and dissolved in some waters. In both cases it has been produced by the oxidation of iron pyrites.

Properties.—This salt is dimorphous, it usually crystallises in bluish-green crystals belonging to the oblique prismatic system, but sometimes in the rhombic system, isomorphous with zincic, manganous, &c., sulphates. It may also be obtained in crystals containing 2, 3, 4, or 5 molecules of water. It is soluble in 1·64 parts of water at 10°, and in 0·3 part at 100°; it is very little soluble in alcohol. When perfectly dry the crystals oxidise but very slowly in dry air, when moist or exposed to the action of moist air they oxidise rapidly. When heated the crystals melt in their water of crystallisation and at a temperature of 280°, air being excluded, yield white anhydrous sulphate. This, when heated more strongly, breaks up into sulphurous anhydride, sulphuric anhydride, and ferric oxide (see Nordhausen sulphuric acid, p. 163). With the sulphates of potassium and ammonium it forms crystallisable double salts. The aqueous solution of ferrous sulphate absorbs nitric oxide yielding a deep brown solution (see p. 121).

Preparation.—1. By dissolving iron in dilute sulphuric acid. 2. By the oxidation of pyrites in the presence of moisture. 3. By the action of scrap iron on solution of copper sulphate.

Ferrous Chloride (*protochloride of iron*), $Fe\,Cl_2 = 127$.

Properties.—This salt forms colourless six-sided scales fusible at a red heat, and sublimes in an atmosphere of gaseous hydrochloric acid, yielding a gas of a density intermediate between those corresponding to the formulæ $Fe\,Cl_2$ and $Fe_2\,Cl_2$ respectively. It is deliquescent in moist air; it is readily soluble in water and alcohol. The solution readily dissolves nitric oxide. Two hydrates, $Fe\,Cl_2,\ 2\,H_2\,O$, and $Fe\,Cl_2,\ 4\,H_2\,O$ are also known.

Preparation.—*Anhydrous*, by passing chlorine over red hot iron turnings or wire. By dissolving iron in hydrochloric acid and evaporating to dryness out of contact with air. By heating ferric chloride in a current of hydrogen. *Hydrated*, by dissolving iron in hydrochloric acid and evaporating with exclusion of air ($Fe\,Cl_2\,4\,H_2O$); or by exposing an ethereal solution of hydrated ferric chloride to the action of light, the solution becomes colourless, and deposits crystals of $Fe\,Cl_2, 2\,H_2O$.

Ferrous Sulphide, $Fe\,S = 88$. *Specific gravity*, 4·8 (*water* = 1).

Occurrence.—In small quantities in meteoric stones as *troilite.* In deposits from water containing sulphates, iron, and organic matters in the form of hydrated ferrous sulphide.

Properties.—This compound is obtained at a low red heat as a black ferrous mass which melts at a higher temperature, solidifying to a yellowish metallic-looking crystalline mass, having a specific gravity of 4·73. It can be heated even to a white heat without loss of sulphur, if air is excluded. When heated in air it yields at first some ferrous sulphate, but on stronger heating leaves only ferric oxide. It dissolves in dilute sulphuric or hydrochloric acids with evolution of sulphuretted hydrogen. A hydrated ferrous sulphide is found frequently in mud containing organic matters, it is very readily oxidised on exposure to air, with separation of sulphur and production of ferric hydrates.

Preparation.—*Anhydrous and amorphous*, by heating together to a red heat three parts of iron filings and two parts of sulphur. *Crystalline*, by fusing the foregoing and allowing it to solidify. *Hydrated*, by precipitating any iron salt with an alkaline sulphide or sulphide of ammonium. By mixing together iron filings and powdered sulphur and moistening the mixture. In a very short time the mixture becomes warm and evolves much steam, and not unfrequently the mass becomes red hot.

FERRIC SALTS (Fe''').

Ferric oxide yields no carbonate.

Ferric Nitrate, $Fe_2\,(N\,O_3)_6 = 484$.

Iron is not acted on by nitric acid of specific gravity 1·45 and upwards (passive iron), and after having been immersed in such an acid it is not dissolved even by more diluted acid until it has been touched, below the level of the acid, by a more electro-negative metal. Diluted acid, however, dissolves the iron, but if of less specific gravity than 1·073, with production of more or less ferrous nitrate [$Fe\,(N\,O_3)_2$], while, if of specific gravity of 1·115 and upwards, ferric nitrate only is produced. In every case nitrous and nitric oxides, and in the case of the weaker acids nitrate of ammonium as well, are produced.

The salt is employed as a mordant.

Ferric Sulphates.—A number of sulphates of ferric oxide are known of varying composition. The normal sulphate, $Fe_2(SO_4)_3, 9H_2O$, occurs native, as *coquimbite*, crystallised in the hexagonal system. It may be prepared by adding sulphuric acid to a solution of ferrous sulphate, and oxidising by means of nitric acid. The anhydrous salt $[Fe_2(SO_4)_3]$ is white and insoluble in sulphuric acid. This sulphate is isomorphous with sulphate of aluminium, and like this yields double salts with the alkaline or ammonium sulphates of the same constitution as ordinary alum (see p. 246). A hexabasic sulphate, Fe_2SO_6 (p. 163), is known, and various basic ferric sulphates may be prepared.

Ferric Sulphide, $Fe_2S_3 = 208$.

This compound is produced by heating iron with its own weight of sulphur at as low a temperature as possible. It constitutes a yellowish metallic-looking mass of a specific gravity 4·4.

Ferric Disulphide, $FeS_2 = 120$.

This sulphide is dimorphous, and occurs native in two varieties. Crystallised in the regular system, or massive as *iron pyrites*, of brass-like yellow colour and metallic lustre, having a specific gravity of 4·9 to 5·18; or crystallised in rhombic crystals, of specific gravity 4·65 to 4·90, as *marcasite* or *white iron pyrites*, or in radiated globular masses. The former variety is usually permanent even in moist air, whereas the latter variety readily oxidises in moist air, and on this account sometimes induces the ignition of coal containing it. It is not acted on by diluted acids, but hot nitric acid slowly dissolves it. When heated in air it takes fire, yielding sulphurous acid and leaving ferric oxide. Enormous quantities of pyrites are now used in the manufacture of sulphuric acid.

Preparation.—It may be artificially prepared by heating finely divided iron with excess of sulphur to a temperature short of redness.

Magnetic Pyrites, Fe_7S_8, occurs native, massive, or in hexagonal crystals of brownish-yellow metallic lustre. It has magnetic properties.

Ferric Chloride, $Fe_2Cl_6 = 325$. *Vapour density at* 440°, 11·39 (*air* = 1); 162·7 ($H = 1$).

Properties.—This salt crystallises in hexagonal metallic-looking plates; red by transmitted, greenish by reflected light. It begins to sublime at 100°. It is very deliquescent, and is soluble in water, alcohol, and ether. Heated in contact with oxygen it yields ferric oxide and chlorine, in contact with steam ferric oxide and hydrochloric acid.

Preparation.—By passing chlorine over gently heated iron; by heating ferrous chloride in chlorine.

Hydrated ferric chloride may be obtained crystallised with either 6 or 12 molecules of water, according to the concentration and temperature of the solution. The solution is formed by dissolving ferric oxide in hydrochloric acid, or by oxidising a solution of ferrous chloride by means of nitric acid, and adding sufficient hydrochloric acid to dissolve the ferric oxide precipitated.

The solution forms a powerful deodorant and antiseptic. When neutral, or nearly so, it is decomposed in very diluted solutions into ferric hydrate, which is precipitated, hydrochloric acid remaining in solution.

Ferric Phosphate, $Fe\,P\,O_4, 2\,H_2\,O = 187$.

A white precipitate obtained by adding a soluble phosphate to a solution of a ferric salt. The precipitate is insoluble in acetic acid, readily soluble in mineral acids.

General Characters of Iron Salts.—**Ferrous salts** are for the most part green when hydrated, white when anhydrous; they are all soluble either in water or in acids. Their solutions yield with *caustic alkalies* or *ammonia* a white precipitate ($Fe\,O, H_2\,O$) speedily becoming brown; the *carbonates of the alkalies* give a white precipitate of ferrous carbonate ($Fe\,C\,O_3$) somewhat less readily oxidised. *Ammonium sulphide* yields a black precipitate of hydrated ferrous sulphide soluble in dilute acid. *Potassium ferrocyanide* gives a white precipitate, speedily becoming blue on exposure to air; *potassium ferricyanide* yields at once a deep blue precipitate. Oxidising agents speedily convert them into ferric salts.

Ferric salts are either brown or red when hydrated, often white when anhydrous. Many of them are insoluble in water, but mostly soluble in acids. Their solutions yield a brown precipitate of ferric hydrate ($Fe_2\,O_3, 3\,H_2\,O$) with *caustic alkalies or ammonia;* they are reduced to ferrous salts with precipitation of sulphur by *sulphuretted hydrogen;* they yield a black precipitate of ferrous sulphide ($Fe\,S$) with *sulphide of ammonium;* a dark blue precipitate with *ferrocyanide of potassium;* a blood-red coloration with acetates, which is destroyed on boiling, basic ferric acetate being precipitated; a deep blood-red coloration, unaffected by boiling or by hydrochloric acid, with *sulphocyanides;* and a bluish-black precipitate with infusion of gallnuts.

Physiological Action.—Iron and its salts act *internally* as tonics and hæmatinics by their specific and unique action on the blood, and as astringents arresting hæmorrhage; all cause constipation: *externally*, or as injections, ferric salts exert a styptic and astringent action.

COBALT.*

Co = 59. *Specific gravity*, 8·5 *to* 8·7 (*water* = 1). *Melts at a somewhat lower temperature than iron. Dyad to tetrad. Specific heat*, 0·1076.

Occurrence in Nature.—Cobalt belongs to the rarer class of elements. It is found in the metallic state in meteoric iron; the *arsenide* and *sulphide*—*speiss cobalt* ($Co\,As_2$) and *cobalt-glance* ($Co\,As\,S$)—are the two principal ores of the metal; it occurs also as sulphate, carbonate, arsenate, &c.

Properties.—Cobalt is of the colour of iron, very slightly malleable, but very ductile, and of nearly twice the tenacity of iron. It is permanent in dry air at ordinary temperature; it tarnishes slowly in moist air; it oxidises rapidly at a red-heat, and decomposes steam at the same temperature. It is soluble in dilute hydrochloric and sulphuric acids, with evolution of hydrogen; in oil of vitriol, with evolution of sulphurous acid; in nitric acid, with evolution of nitric oxide. In all these cases cobaltous salts are produced.

The metal is not used as such, but some of its compounds, distinguished for their brilliant and permanent blue colour, are used extensively. Cobalt is magnetic, and the metal loses its magnetism only at a white heat.

Preparation.—By reducing purpureo-cobalt chloride ($Co_2\,Cl_6, 10\,N\,H_3$), or any oxide of cobalt, by means of hydrogen at a red heat, and melting the resulting metal in a lime crucible.

The production of cobalt from its ores, which generally contain sulphur, arsenic, nickel, iron, copper, bismuth and other metals, is a somewhat complicated and difficult process, and several have been devised, one of which we may give shortly. The ore is first roasted, whereby much arsenic is eliminated. The roasted ore, known as *zaffre*, is dissolved in hydrochloric acid, with the addition of some nitric acid, and the solution carefully neutralised with milk of lime. This throws down the iron in the form of hydrated sesquioxide, carrying down with it the remaining arsenic as arsenate of iron. The filtrate from this is acidified with hydrochloric acid, and sulphuretted hydrogen passed into the solution, which throws down copper, bismuth, and allied metals. From the clear filtrate from this precipitate the cobalt is thrown down in the form of hydrated sesquioxide, cobaltic

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*German, *Kobalt*, from *Kobold*, derived from Latin, *cobalus;* Greek, Κόβαλος, a *goblin*, meaning a sprite or goblin of the mine; an ancient fanciful name of mining origin applied later on to certain minerals containing this metal, and finally adopted as its name.

oxide ($Co_2 O_3, 3 H_2 O$), by the careful addition of bleaching powder, using enough to precipitate the cobalt only, but not the nickel. The hydrated oxide thus obtained is ignited, when it becomes converted into cobalto-cobaltic oxide ($Co_3 O_4$), and is used in that form for the production of blue glass and smalt. It still, however, contains nickel, and generally iron, to free it from which it is once more dissolved in hydrochloric acid, the solution is evaporated to a small bulk, and chloride of ammonium and excess of ammonia added. The precipitate of oxide of iron, if any, is filtered off, and the filtrate allowed to stand until such time, generally some days, that a portion of it when mixed with excess of hydrochloric acid no longer turns blue. Excess of hydrochloric acid is now added to the whole, and the solution boiled and evaporated, when nearly the whole of the cobalt separate in the form of purpureo-cobalt chloride ($Co_2 Cl_6 10 N H_3$).

OXIDES OF COBALT.

Cobalt forms several oxides, but only the monoxide yields stable salts.

Cobaltous Oxide, . .	$Co O$.
Cobaltic Oxide, . .	$Co_2 O_3$.
Cobalto-cobaltic Oxide, .	$Co_3 O_4$.

Cobaltous Oxide (*cobalt monoxide*), $Co O = 71$.

Properties.—A green-brown to brown powder, which oxidises at ordinary temperatures, but very slowly; more rapidly at slightly elevated temperatures. It is readily soluble in acids, yielding stable cobaltous salts, in which the metal is a dyad. It imparts a magnificent blue colour to a silicate (*smalt*) or to the borax bead.

Preparation.—1. By heating cobaltous carbonate, air being excluded. 2. By heating cobalto-cobaltous oxide in a current of carbonic anhydride. 3. The oxide is obtained as a hydrate ($Co H_2 O_2 = Co O, H_2 O$) in the form of a blue precipitate, changing to violet or red on standing, by the addition of potassium hydrate to a solution of cobaltous chloride, air being excluded.

Cobaltic Oxide (*cobalt sesquioxide*), $Co_2 O_3 = 158$.

Properties.—A brown to black powder, which dissolves in cold acids, yielding brown solution of cobaltic salts, in which the double atom is hexad. On standing, or more rapidly on boiling, these solutions are decomposed, and a cobaltous salt formed. In the case of hydrochloric acid, chlorine is evolved, while in the case of an oxygen acid, oxygen is liberated, the sesquioxide behaving rather like a peroxide than a sesquioxide. A hydrate of this oxide ($Co_2 H_6 O_6 = Co_2 O_3, 3 H_2 O$) is obtained by precipitating a cobaltous salt with a solution of an alkaline hypochlorite or of bleaching powder.

Cobalto-Cobaltic Oxide, $Co_3 O_4 = 241$. $[Co O, Co_2 O_3]$.

All oxides of cobalt when heated for some time to redness in air yield this oxide.

COBALTOUS SALTS.

Cobaltous Carbonate, $Co C O_3 = 119$.

The normal carbonate may be prepared by precipitating a solution of cobaltous chloride at a temperature of 140°, with a solution of sodium bicarbonate, saturated with carbonic anhydride. Various basic carbonates may be obtained by precipitating solutions of cobaltous chloride, with neutral alkaline carbonates at or near the boiling point. A hydrated carbonate, *Remingtonite*, is found native.

Cobaltous Nitrate, $Co (N O_3)_2 6 H_2 O = 183 + 108 = 291$. *Specific gravity*, 1·83 (*water* = 1).

This salt crystallises in red deliquescent prisms of the oblique prismatic system, very soluble in water. It may be prepared by dissolving either the metal, the oxide, or the carbonate in nitric acid. It is used as a reagent in the laboratory.

Cobaltous Sulphate, $Co S O_4, 7 H_2 O = 155 + 126 = 281$. *Specific gravity*, 1·92 (*water* = 1).

This salt crystallises in dark-red crystals isomorphous with ferrous sulphate. It may be prepared by dissolving the oxide or carbonate in sulphuric acid. It forms double salts with the alkaline sulphates.

Cobaltous Chloride, $Co Cl_2, 6 H_2 O = 130 + 108 = 238$. *Specific gravity*, 1·84 (*water* = 1).

This salt crystallises in dark-red oblique prisms, which at a temperature of 120° lose part of their water and become blue ($Co Cl_2 2 H_2 O$), becoming anhydrous at 140°. By writing with a dilute solution of cobaltous chloride on paper, the writing after drying at ordinary temperature is invisible, or nearly so; on gently heating the paper, the writing becomes blue and distinctly visible, but fades away again at ordinary temperature in moist air (sympathetic ink).

The salt may be prepared by dissolving the metal or any of the oxides in boiling hydrochloric acid, and evaporating to crystallisation.

Cobaltous Sulphide, $Co S = 91$.

This compound is found native (*specific gravity*, 5·45). It may be artificially obtained as a black hydrate, by precipitating the acetate with sulphuretted hydrogen or any other cobaltous salt with sulphide of ammonium. Several other sulphides corresponding to those of iron are known.

Silicates of Cobalt.—Cobaltous oxide dissolves in melted acid silicates yielding a glass of magnificient blue colour, which, when ground, is known as *smalt.* The blue colour is not affected by acid or alkalies, and is permanent in air.

Ammonium Compounds of Cobalt.—Cobalt yields a large series of compounds with ammonia and its salts, of various colours and more or less complex constitution, but which may all be regarded as ammonium salts, in which hydrogen is replaced either by dyad or pseudo-hexad cobalt. They are known under the general name of cobaltamines.

General Character of Cobaltous Salts.—Cobaltous salts are generally pink or red when hydrated, blue when anhydrous or slightly hydrated. They yield with *caustic alkalies* and *ammonia* a blue precipitate, soluble in excess of the latter with a brownish-red colour. *Potassium cyanide* forms a yellowish-brown precipitate, soluble in excess, in which solution, after boiling, hydrochloric acid produces no precipitate (distinction from nickel). Sulphuretted hydrogen yields no precipitate in presence of a strong acid, sulphide of ammonium gives a black precipitate of sulphide. The salts impart a magnificent blue colour to the borax bead, both in the oxidising and in the reducing flame.

NICKEL.*

Ni = 59. *Specific gravity*, 8·8 *to* 9. *Melts somewhat more readily than iron. Dyad to hexad. Specific heat*, 0·1082.

Occurrence in Nature.—Nickel, though belonging to the less frequently occurring elements, is found in considerable deposits, chiefly as *arsenide* in *kupfer-nickel* (Ni As); it is also found associated with cobalt in *speiss cobalt* and other minerals, and as sulphide, silicate, arsenate, &c. The metal is an essential constituent of *meteoric iron* (see iron, p. 273).

Properties.—Nickel is a white or almost white metal possessing considerable lustre, malleable and ductile, and of great tenacity (one and a-half times that of iron). It is permanent in dry, and almost so in moist air. It is soluble in hydrochloric and sulphuric acids, with

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* The mineral *kupfer-nickel* (Ni As) was so-called on account of its resemblance to copper; the term *nickel* implying *false* or *base*, and used as a contemptuous epithet in some parts of Germany, was afterwards retained for the new metal.

evolution of hydrogen; readily soluble in nitric acid. It decomposes water at a red heat. The metal is used chiefly alloyed with zinc and copper (*German silver*), or as a coating on other metals produced by precipitating the metal from the double cyanide, by means of the galvanic current. The metal is magnetic, but loses its magnetism at a temperature of 350°.

Preparation.—1. By heating the oxide with carbon, or in hydrogen. 2. By heating the oxalate out of contact with air, and melting the resulting metallic powder in a lime crucible. In order to obtain the pure oxide the ores are treated as described under cobalt (p. 284); the solution from which the cobalt has been precipitated by bleaching powder is treated with milk of lime, the precipitated oxide of nickel is ignited, treated with hydrochloric acid to remove lime, and the oxide reduced as above.

Oxides and Salts of Nickel.—The compounds of nickel with oxygen, chlorine, sulphur, as well as the salts of the monoxide, are prepared in a manner exactly like the corresponding cobalt compounds, and are closely analogous to the same. Nickel, however, yields no corresponding ammonium compounds.

The sulphate, $Ni\,S\,O_4, 7\,H_2\,O$, crystallises in rhombic prisms, isomorphous with magnesium sulphate.

General Characters of Nickel Salts.—The hydrated salts are green, the anhydrous yellow. *Caustic alkalies* and *ammonia* produce a pale-green precipitate, $Ni\,(H\,O)_2$, soluble in excess of the latter with a deep blue colour. *Sulphide of ammonium* yields a black precipitate, slightly soluble in excess, forming a brown solution. *Cyanide of potassium* yields a green precipitate, soluble in excess, with formation of a double salt, from which solution, even after boiling, acids precipitate cyanide of nickel, and sodic hypochlorite black hydrated nickelic oxide (distinction from cobalt salts).

Nickel salts colour the borax bead pinkish-brown in the oxidising flame, in the reducing flame the bead becomes grey and cloudy from reduced nickel.

CHROMIUM.*

Cr = 52·4. *Specific gravity*, 7·015 (*water* = 1). *Specific heat*, 0·100.
Melts at a higher temperature than platinum. Dyad to hexad.

Occurrence in Nature.—Chromium belongs to the less common metals; its chief occurrence is as *chrome-ironstone* ($Fe\,O,\ Cr_2\,O_3$); it is also

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* Χρῶμα, *colour;* in allusion to its many-coloured compounds.

found as chromate of lead in the mineral *crocoisite* ($PbCrO_4$); it is a constituent of many minerals, and when present always acts as a colouring agent.

Properties.—Chromium in the metallic state is steel-grey to white in colour; it crystallises in the regular system; it is very hard (approaching the hardness of *corundum*) and very brittle. It requires a higher temperature for fusion than platinum (above 2,000°). It is permanent in air at ordinary temperatures, but oxidises slowly at a red heat, rapidly in contact with nitre. It decomposes water at a red heat. It is readily soluble in warm sulphuric acid, or in cold hydrochloric acid, with evolution of hydrogen. It is scarcely acted on by nitric acid.

Preparation.—1. By reducing chromic oxide (Cr_2O_3) by means of lamp-black at the highest temperature of a wind-furnace. 2. By heating to a white heat chromic chloride (Cr_2Cl_6) mixed with chlorides of potassium and sodium, together with granulated zinc, placed in alternate layers in a Hessian crucible; the resulting regulus being treated first with cold and afterwards with warm nitric acid to remove the zinc. 3. By reducing chromic chloride by means of potassium or sodium. 4. By electrolysis of a solution of chromium chloride.

OXIDES OF CHROMIUM.

Chromium forms several oxides—

Chromous Oxide,	CrO.
Chromic Oxide,	Cr_2O_3.
Trichromic Tetroxide (?),	Cr_3O_4.
Chromic Peroxide (?),	CrO_2.
Chromic Anhydride	CrO_3.
Perchromic Anhydride (?),	CrO_7.

Chromous Oxide (*chromium monoxide*), $CrO = 68{\cdot}4$.

This oxide is known only in the hydrated condition, CrH_2O_2, or CrO, H_2O, in which condition it is obtained as a brownish-yellow precipitate, by the addition of caustic potash to a solution of chromous chloride ($CrCl_2$), with exclusion of oxygen and drying in an atmosphere of hydrogen over sulphuric acid. When once dry it does not oxidise further in dry air, but does so rapidly when moist. The hydrate, on heating, yields chromic oxide, water and hydrogen—$2CrH_2O_2 = Cr_2O_3 + H_2O + H_2$. It is difficultly soluble in acids, scarcely soluble in nitric acid; the solution contains a chromic salt (see below).

Chromic Oxide (*sesquioxide of chromium*), $Cr_2\ O_3 = 252{\cdot}8$.

Properties.—The amorphous oxide is a dull or bright green powder, or it may be obtained crystalline in black, iridescent, hexagonal crystals (green when powdered), isomorphous with the corresponding oxides of iron and aluminium, and almost as hard as *cornudum* ($Al_2\ O_3$); it is fusible before the blowpipe without decomposition. The amorphous oxide when gently heated, so that it is not caused to glow, is soluble in acids, but not very readily; after strongly heating it is almost insoluble, but is slowly dissolved in boiling oil of vitriol. It is readily oxidised by fusion with nitre to the trioxide. The crystallised oxide is almost insoluble in acids, and scarcely acted on by nitre.

Mixed with charcoal and heated to redness in a current of chlorine it yields anhydrous chromic chloride ($Cr_2\ Cl_6$).

Chromic oxide unites with basic oxides forming compounds, which may be regarded as salts of a chromous acid, $H_2\ Cr_2\ O_4$, called *chromites.* Thus, chromic oxide, when precipitated by fixed alkalies, always retains alkali which cannot be removed by washing. Other compounds of this oxide are, however, more definite; they correspond to the *aluminates* ($M\ O,\ Al_2\ O_3$), and to *magnetic oxide of iron* ($Fe\ O,\ Fe_2\ O_3$), and one of them—viz., *chrome-ironstone* ($Fe\ O,\ Cr_2\ O_3$; $Fe\ Cr_2\ O_4$) forms the principal ore of chromium.

Chromic oxide imparts a beautiful deep green colour to glass.

Preparation—(*a*) *Amorphous.*—1. By heating ammonium bichromate [$(N\ H_4)_2\ Cr\ O_4,\ Cr\ O_3$]. 2. By heating potassium bichromate with ammonium chloride, and extracting the heated mass with water. 3. By heating chromic hydrate. (*b*) *Crystalline.*—1. By melting the amorphous oxide in the oxyhydrogen blowpipe and cooling. 2. By strongly heating oxychloride of chromium.

Chromic Hydrates.—Chromic oxide forms several hydrates. The hydrate $Cr_2\ O_3,\ 7\ H_2\ O$ is thrown down as a pale bluish-green precipitate on addition of ammonia to a chromic salt; it is soluble on warming in strong ammonia, forming a violet solution. It may be dried over oil of vitrol; if dried *in vacuo* over oil of vitrol, it retains four molecules of water only ($Cr_2\ O_3,\ 4\ H_2\ O$); when dried at 220° in a current of hydrogen, it retains one molecule only ($Cr_2\ O_3,\ H_2\ O$). The hydrate obtained by adding excess of caustic alkali solution to a chromic salt (whereby the hydrate first thrown down is redissolved), and boiling the solution, always contains alkali. A hydrate containing two molecules of water is known as *Guignet's green*, and is obtained by heating potassium dichromate with boric acid, and washing the resulting mass with water. A solution of a hydrate in water, analogous to *dialysed iron* (p. 277), is also obtainable. All the hydrates are soluble in acids, but not very readily.

Trichromic Tetroxide, $Cr_3 O_4 = 221{\cdot}2$.

This oxide is obtained as a hydrate in the form of a reddish-brown precipitate by adding a solution of potassium hydrate to a solution of chromous chloride, with partial access of air. It is obtained anhydrous by decomposing an aqueous solution of chromous chloride by a weak electric current. It readily absorbs oxygen, and becomes converted into chromic oxide.

Chromic Peroxide (*chromyl*), $Cr O_2 = 84{\cdot}4$.

This is a brown powder obtained by reduction of chromic acid. Its properties are very little known.

Chromic Anhydride (*chromic trioxide*), $Cr O_3 = 100{\cdot}4$. *Specific gravity*, 2·75 (*water* = 1). *Melting point, about* 300°.

Properties.—This oxide crystallises in magnificent dark-red needles or prisms belonging to the rhombic system, which are very soluble in water, yielding a red solution; it is also soluble in diluted or concentrated sulphuric acid, but almost insoluble in an acid containing about 16 to 17 per cent. of water. It may be melted without decomposition, but at a temperature of 250° it breaks up into chromic oxide and oxygen. Chromic acid, $H_2 Cr O_4$, is not known by itself, but a series of salts are known corresponding to such a dibasic acid, which salts are amorphous with the corresponding sulphates. It acts as a powerful oxidising agent, particularly at a somewhat elevated temperature, in presence of sulphuric acid, becoming reduced to chromic oxide. A strong aqueous solution of chromic anhydride acts as a powerful corrosive and disinfectant; in very dilute solutions it has a remarkable hardening effect on nervous tissues. Its salts are poisonous.

Perchromic Acid.—When peroxide of hydrogen is added to chromic acid or to a chromate acidulated with sulphuric acid, the liquid becomes blue, and on shaking it up with ether the compound dissolves in the ether, which acquires a deep blue colour. This blue compound is possibly perchromic acid ($H_2 Cr_2 O_8$; $H Cr O_4$). The solution is very unstable, and yields chromic anhydride on evaporation.

SALTS OF CHROMIUM.

Chromous Salts.—All chromous salts show great affinity for oxygen, and are in consequence very unstable; they cannot be formed by dissolving chromous oxide in acids (see p. 289), but may be obtained by precipitating a solution of chromous chloride by the corresponding potassium salt. The sulphate, $Cr\,S\,O_4$, may be obtained by dissolving the metal in sulphuric acid.

A solution of the chloride, $Cr\,Cl_2$, may be obtained by dissolving the metal in hydrochloric acid. It yields a blue solution which rapidly absorbs oxygen.

Chromic Salts.—Chromic oxide yields two kinds of salts, one of which dissolves with a green, the other with a violet colour; as a rule the latter only are crystallisable. At ordinary temperatures the green variety changes gradually to the violet, while at a boiling temperature the violet variety changes rapidly into the green. In these salts the double atom of chromium is hexad.

Chromic Sulphate, $Cr_2\,(S\,O_4)_3\,15\,H_2\,O = 392{\cdot}8 + 270 = 662{\cdot}8$.

This salt may be obtained by dissolving chromic hydrate in sulphuric acid. The solution is at first green, but after a while changes to violet and deposits violet-blue, regular octahedra of the above salt. The salt is chiefly of interest because it yields with sulphate of potassium a double sulphate (chromium alum) analogous to ordinary alum (p. 246).

Chrome Alum, $Cr\,K\,(S\,O_4)_2\,12\,H_2\,O$ or $Cr_2\,(S\,O_4)_3\,K_2\,S\,O_4,\,24\,H_2\,O$.

By acting on a solution of dichromate of potassium and sulphuric acid by various reducing agents and crystallising in the cold, ruby-red, regular octahedra isomorphous with alum are obtained. The crystals dissolve in water with a violet-blue colour, which on heating changes to green, and then no longer crystallises. On standing, at ordinary temperatures, the colour slowly changes again to violet-blue, and the salt again crystallises.

Chromic Chloride, $Cr_2\,Cl_6 = 317{\cdot}4$.

Properties.—Peach-blossom coloured scales, which, when pure, are almost insoluble in water, but dissolve readily in presence of even a trace of chromous chloride, yielding a green solution; this same solution is obtained by dissolving chromic hydrate in hydrochloric acid; the solution on evaporation over oil of vitriol yields green needle-like crystals of $Cr_2\,Cl_6\,12\,H_2\,O$. Heated in air the anhydrous chloride breaks up into chromic oxide and chlorine, the hydrated into oxychloride and hydrochloric acid.

Preparation.—*Anhydrous*, by heating a mixture of chromic oxide and charcoal in a current of chlorine; by heating the hydrated chloride in a current of hydrochloric acid. *Hydrated*, by dissolving the hydrated oxide in hydrochloric acid, and evaporating over oil of vitriol to crystallisation.

Chromates.—Chromates are distinguished for their beautiful colour, and some are on that account used as pigments. They all act as powerful oxidising agents. The normal salts correspond in composition to the sulphates, with which they are isomorphous; the acid salts are nearly always anhydrous, and correspond to the pyrosulphates.

Potassic Chromate, $K_2\,Cr\,O_4 = 194{\cdot}4$. *Specific gravity*, 2·7 (*water* = 1).

Properties.—Pale-yellow crystals belonging to the right prismatic or rhombic system, isomorphous with sulphate of potassium. The salt is soluble in twice its weight of cold water, much more soluble in hot water. When heated it first turns red, then melts without decomposition. The solution is alkaline, and has a pale-yellow colour, which is changed to red, with formation of dichromate, by all acids, even carbonic acid.

Preparation.—By adding an excess of caustic potash to a solution of the dichromate of potassium and evaporating to crystallisation.

Dichromate of Potassium (*potassium bichromate*), $K_2\,Cr_2\,O_7 = 294{\cdot}8$. *Specific gravity*, 2·68 (*water* = 1). $[K_2\,Cr\,O_4\,,\,Cr\,O_3]$.

Properties.—Garnet red crystals belonging to the doubly oblique prismatic system. The crystals are soluble in ten times their weight of cold, more soluble in hot water. The solution is red, slightly acid, and turns yellow on addition of an alkali. When heated the salt fuses without decomposition, but at a white heat it breaks up into normal chromate, chromic oxide, and oxygen. It acts as a strong oxidising agent, particularly in presence of sulphuric acid, and is often employed as such; it is also used in calico printing and in photography.

This salt corresponds to sodium pyrosulphate (p. 163).

Preparation.—Chrome-iron ore is first roasted, then finely ground, and mixed with potash and lime, the mixture is dried and then heated to bright redness in the oxidising flame of a reverberatory furnace. The heated mass, which is not fused owing to the addition of lime, is extracted with a minimum of boiling water, a quantity of sulphuric acid sufficient to neutralise half the potassium present is added and the solution allowed to crystallise.

$$2\,K_2\,Cr\,O_4 + H_2\,S\,O_4 = K_2\,S\,O_4 + K_2\,Cr_2\,O_7 + H_2\,O.$$

Ammonic Chromates.—The salts $(NH_4)_2\,CrO_4$ and $(NH_4)_2\,CrO_4, CrO_3$, are obtained by adding ammonia in the required quantity to an aqueous solution of chromic anhydride. The salts resemble the corresponding potassium salts, but when heated break up into chromic oxide, water, and nitrogen, and in the case of the normal salt also give off ammonia. The dichromate on heating gently becomes incandescent, swells up, and leaves a bulky mass of chromic oxide closely resembling green tea in appearance.

Barium Chromate, $Ba\,Cr\,O_4 = 253{\cdot}4$. *Specific gravity*, 4·3 (*water* = 1).

This salt is very insoluble in water; it is obtained as a yellow precipitate, insoluble in acetic acid, on adding potassium chromate or dichromate to a soluble barium salt (distinction from strontium).

Lead Chromate (*plumbic chromate*), $Pb\ Cr\ O_4 = 323{\cdot}4$. *Specific gravity*, 6·0 (*water* = 1).

Occurs native as *crocoisite* in oblique prismatic crystals, having a specific gravity of 5·9 to 6·1. It is obtained as a bright yellow precipitate when potassium chromate or dichromate solution is added to a solution of a lead salt, and is much used as a pigment under the name of chrome-yellow. When heated it fuses without decomposition, and solidifies to a crystalline mass. Combustible matters heated with it are completely oxidised or burnt, and the salt is used in organic analysis for the estimation of carbon.

A basic lead chromate may be obtained by boiling the foregoing salt with caustic soda or by fusing it with nitre. It forms a red powder, and is used as a pigment under the name of chrome-red.

Chromate of Silver (*argentic chromate*), $Ag_2\ Cr\ O_4 = 332{\cdot}4$. *Specific gravity*, 5·7 (*water* = 1).

Obtained as a red precipitate by adding a solution of neutral potassic chromate to a neutral solution of a silver salt. The precipitate, which is soluble both in acids and alkalies, is used as an indicator in the titration of chlorides.

Chromyl Dichloride (*chlorochromic acid*), $Cr\ O_2\ Cl_2 = 155{\cdot}4$. *Specific gravity of vapour*, 77·75 ($H = 1$).

Properties.—Heavy oily liquid of deep red colour boiling at 118° (specific gravity, 1·92, $H_2\ O = 1$), yielding a dark brown vapour very much resembling bromine in appearance. It fumes in contact with moist air; water decomposes it into hydrochloric and chromic acids. It is an extremely powerful oxidising agent, and many combustible substances (inorganic and organic) explode or ignite when brought into contact with it.

Preparation.—By acting with sulphuric acid on a fused mixture of 10 parts of chloride of sodium with 12 parts of bichromate of potassium and distilling; the brown vapours are condensed in a cool receiver. The production of this compound forms the most delicate test for the detection of traces of chlorides in presence of bromides or iodides.

Chlorochromates.—By gently warming a mixture of 3 parts of potassium bichromate, to which a little water has been added with 4 parts of hydrochloric acid until chlorine begins to be evolved, and allowing the solution to cool, red plates of so-called chlorochromate of potassium crystallise out—

$$K_2\,Cr_2\,O_7 + 2\,H\,Cl = 2\,Cr\,O_3\,Cl\,K + H_2\,O.$$

The same compound is produced by carefully dropping chromyl dichloride into an aqueous solution of potassic chromate, to which a little acetic acid has been added.

$$Cr\,O_2\,Cl_2 + K_2\,Cr\,O_4 = 2\,Cr\,O_3\,Cl\,K.$$

The two preceding compounds correspond respectively to sulphuryl chloride, $S\,O_2\,Cl_2$, and sulphuric oxychlorohydrate, $S\,O_2\,Cl\,H\,O$.

Sulphide of Chromium (*chromic sulphide*), $Cr_2\,S_3 = 200{\cdot}8$.

No sulphide of chromium can be obtained in the wet way (since it is decomposed by water with formation of chromic hydrate and hydrogen sulphide), but may be formed by the direct union of the elements; it is a grey powder of metallic lustre.

Chromic Nitride, $Cr_2\,N_2 = 132{\cdot}4$.

Formed by passing nitrogen over red hot chromium, or by the action of ammonia on chromic chloride.

General Character of Chromium Compounds.—All compounds of chromium, when fused with carbonate of soda and nitre, yield a yellow mass of chromate; and they impart a green colour to the borax bead.

Chromous Compounds.—These are strong reducing agents, and are rapidly converted into chromic compounds.

Chromic Compounds.—The solutions of these salts are violet or green; the violet solutions become green on boiling *Caustic alkalies* give a green precipitate ($Cr_2\,O_3\,x\,H_2\,O$) soluble in excess to a deep green solution, but reprecipitated on boiling; *ammonia* yields also a bluish-green precipitate, slightly soluble in excess of dilute ammonia solution, but soluble on warming with strong ammonia to a violet solution. *Ammonium sulphide* precipitates chromic hydrate, sulphuretted hydrogen being evolved.

Chromates.—The solutions are yellow when neutral, red when acid. Reducing agents change the colour to green, and the solution then contains a chromic salt. A solution of acetate of lead yields a bright yellow; one of nitrate of silver, a red precipitate.

MOLYBDENUM.*

Mo = 96. *Specific gravity*, 8·6 (*water* = 1). *Specific heat*, 0·0722. *Pentad.*

Occurrence in Nature.—Molybdenum is not found free in nature, but occurs as sulphide in *molybdenite* ($Mo\,S_2$), as molybdate of lead in *wulfenite* ($Pb\,Mo\,O_4$), and as trioxide in *molybdic ochre* ($Mo\,O_3$), and some other rare minerals; it is also found accompanying some ores of iron.

Properties.—Molybdenum is a silver white, bright, very hard metal which tarnishes slowly in air; it decomposes water at a red heat; it is fusible only at a very high temperature; heated very strongly in air it burns to trioxide ($Mo\,O_3$). It is soluble in nitric acid,

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* μολυβδος, lead; probably in allusion to the colour of its sulphide.

which oxidises it to molybdic acid, $H_2 Mo O_4$, and in strong sulphuric acid, not in hydrochloric acid.

Preparation.—By reducing the trioxide in a current of hydrogen, or by heating the trioxide with charcoal at a very high temperature.

Oxides and Salts.—Molybdenum forms several oxides, $Mo O$, $Mo_2 O_3$, $Mo O_2$, $Mo O_3$; the trioxide forms several hydrates (molybdic acids), giving rise to salts (molybdates) of the most complex composition, but also forms the hydrate, $Mo O_3, H_2 O = H_2 Mo O_4$, of which many salts are known. The ammonium molybdate, which is used as a laboratory reagent, is not the normal salt, $(N H_4)_2 Mo O_4$, but has the composition $(N H_4)_6 Mo_7 O_{24}, 4 H_2 O$. It crystallises in monoclinic prisms; for use as a reagent it must be dissolved in strong ammonia solution, as it is decomposed by water; the solution is almost exclusively employed as a test for phosphoric acid (p. 195), with which it forms a yellow precipitate, having the composition, $12 Mo O_3, P O_4 (N H_4)_3, 1\frac{1}{2} H_2 O$, which is insoluble in nitric acid, but soluble in alkalies.

Of the salts of molybdenum, the chlorides are numerous and best known, they are $Mo Cl_2$, $Mo_2 Cl_6$, $Mo Cl_4$, $Mo Cl_5$, and these form numerous crystallisable compounds with other salts. The compounds of molybdenum are by no means thoroughly investigated as yet.

Distinguishing Tests.—Solutions of compounds of molybdenum, give with zinc and hydrochloric acid (nascent hydrogen) a blue coloration, changing to green and brown (like tungsten solutions); with hydrogen sulphide they yield a brown precipitate of trisulphide, soluble in ammonium sulphide. Molybdates may be detected in this way and by numerous other reactions. A special test is said to be the formation of a blue liquid when molybdic acid or a molybdate is first heated with concentrated sulphuric acid, and then alcohol added and ignited (distinction from tungsten).

TUNGSTEN.*

(*Wolfram*) $W = 184$. *Specific gravity*, 19·129 (*water* = 1). *Specific heat*, 0·0334.

Occurrence in Nature.—This comparatively rare metal is not found in the free state, but as tungstate in the mineral *Wolfram* [$(Mn Fe) W O_4$], in *scheelite* ($Ca W O_4$), and in *scheelitine* ($Pb W O_4$), more rarely as trioxide in *Wolfram ochre* ($W O_3$), &c.

Properties.—Tungsten is of an iron-grey colour; it is almost infusible; it remains unchanged in air at ordinary temperatures, but if heated in a finely divided state in contact with air it takes fire and burns to trioxide ($W O_3$). It is scarcely attacked by acids, slowly by nitric acid; *aqua regia* converts it into trioxide, which is insoluble in acids.

Tungsten is said to add materially to the hardness of steel, and to increase its magnetic properties greatly.

Preparation.—By the reduction of the trioxide with hydrogen or with carbon at a high temperature.

Oxides and Salts.—Tungsten forms three oxides, $W O_2$, $W O_3$, and $W_2 O_5$ (?). The trioxide, like the corresponding molybdenum compound, forms several hydrates, a monohydrate, $H_2 W O_4$, and others of a very complex nature called *tungstic acids*, forming salts called *tungstates*. *Sodium paratungstate*, $Na_{10} W_{12} O_{41}, 28 H_2 O$, is a commercial product, and used for rendering light-woven materials uninflammable, and as a mordant in dyeing. Like molybdic acid, tungstic acid also forms an insoluble *phospho-tungstic acid*.

Tungsten forms several chlorides, $W Cl_2$, $W Cl_4$, $W Cl_5$, $W Cl_6$.

Distinguishing Tests.—Zinc and hydrochloric acid (nascent hydrogen) give with a solution of a tungstate a blue coloration, becoming copper-red. Hydrogen sulphide produces no precipitate in acid solutions, but ammonium sulphide, when mixed with a solution of a tungstate, yields a brown precipitate ($W S_3$) on acidulating with hydrochloric acid. Tungsten compounds give with microcosmic salt a blue bead in the reduction flame, or blood-red if iron is present.

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* Swedish, *tungsten*, heavy stone.

URANIUM.*

U = 240.† *Specific gravity*, 18·3 (*water* = 1). *Specific heat*, 0·0276.

Occurrence in Nature.—Uranium occurs in a few minerals only, and is a comparatively rare metal; its chief occurrence is as *oxide*, in an impure form, in *pitchblende* [$U_3 O_8 = U O_2, 2 U O_3$]; it is also found as phosphate in *uranite* [$Ca_3 (P O_4)_2, 2 (U O_2)_3 (P O_4)_2, 30 H_2 O$], and as *carbonate* in *liebigite* [$Ca CO_3, (U O_2) C O_3, 20 H_2 O$?], and in a number of rare minerals.

Properties.—The metal has a steel-grey colour, is brittle, and on exposure to air becomes slightly tarnished, but at a red heat burns brilliantly to urano-uranic oxide, $U_3 O_8$. It is soluble in dilute acids.

Preparation.—By acting on uranous chloride ($U Cl_4$) with sodium at a red heat.

Oxides and Salts.—Uranium forms two definite oxides, $U O_2$ and $U O_3$, and a number of intermediate oxides which are not well known. The dioxide acts as a basic oxide, and forms a number of salts—*e.g.*, uranous chloride, $U Cl_4$, uranous sulphate, $U (S O_4)_2$, but it also acts as a dyad radical, combining with acids to form salts, which are termed salts of uranyl, thus, uranyl chloride $(U O_2) Cl_2$, uranyl sulphate $(U O_2) S O_4$; acetate of uranyl $(U O_2) (C_2 H_3 O_2)_2$ is used in the laboratory as a reagent for the detection and estimation of phosphoric acid, with which it forms in the presence of ammonium chloride an insoluble greenish-yellow precipitate—ammonio-phosphate of uranyl $(U O_2) N H_4 P O_4$.

The trioxide is an acid-forming oxide, and forms salts which correspond to the dichromates having the general formula, $M_2 U_2 O_7 = M_2 U O_4, U O_3$.

Distinguishing Tests.—Uranium salts are green or yellow, they impart a yellowish-green colour to glass, rendering it highly fluorescent. With borax or microcosmic salt, they yield a green bead.

TIN.‡

(*Latin*, *Stannum*) *Sn* = 118. *Specific gravity*, 7·3 (*water* = 1). *Specific heat*, 0·0562. *Melting point*, 232·7°. *Boiling point*, *between* 1450° *and* 1600°. *Tetrad.*

Occurrence in Nature.—This metal is very rarely found in the free state, and is not very widely diffused, but occurs locally in immense deposits as *oxide* in the mineral *tin-stone* or *cassiterite* ($Sn O_2$) in various parts of the world, most notably in Cornwall, whose tin mines have been worked from the earliest times. The ore occurs in veins running through primitive rocks (granite, porphyry, &c.); owing to the natural disintegration of these rocks the ore is also found in loose nodules (*stream-tin*) of greater or less size, rounded by the action of water, and free from compounds of iron, copper, arsenic, and antimony, which are present in the vein ore. Other notable localities in which tin-stone deposits are found are in the Erzgebirge, in Bretagne, in

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* So called by Klaproth in 1789, after the then newly discovered planet, Uranus.

† The atomic weight of uranium, formerly 120, has lately been doubled from theoretical considerations, on account of the analogy of the element to chromium

‡ Anglo-saxon, *tin*; the same word in Icelandic and Danish. German, *zinn*. Swedish, *tenn*.—*Skeat*.

Gallicia, in the island of Banca and the Malay peninsula, in Peru, and especially in Queensland and New South Wales, where very extensive deposits have been recently discovered.

Tin is also found, but rarely, as sulphide, and is a constituent of a few minerals of unfrequent occurrence.

Properties.—Tin is a bright silver-white metal; it is harder than lead, but softer than gold, very malleable, but at higher temperatures (about 200°) is very brittle; it is comparatively ductile, but possesses very little tenacity; it melts at 233°. It has a crystalline structure, and emits a peculiar crackling-sound when bent. It may be obtained in prismatic crystals by fusing and partial solidification. At ordinary temperatures it remains unaltered on exposure to air; when strongly heated in air it becomes covered with a film of oxide, and at a white heat ignites, burning with a bright flame to oxide.

Tin is soluble in hydrochloric acid, forming stannous chloride ($Sn\,Cl_2$), and in sulphuric acid, forming stannous sulphate ($Sn\,S\,O_4$); nitric acid acts on it with great energy; in dilute nitric acid it dissolves, forming stannous nitrate * [$Sn\,(N\,O_3)_2$], or with rather stronger acid, stannic nitrate [$Sn\,(N\,O_3)_4$?], which last compound rapidly decomposes, hydrated stannic acid ($H_2\,Sn\,O_3 + aq.$) being precipitated in a gelatinous form; with moderately strong nitric acid the metal is converted into an insoluble white powder, generally regarded as so-called metastannic acid ($H_{10}\,Sn_5\,O_{15} = 5\,H_2\,Sn\,O_3$). Concentrated nitric acid is without action on tin. *Aqua regia* dissolves tin, and converts it into the tetrachloride ($Sn\,Cl_4$).

Owing to its stability in air, its malleability, its low melting point, and other characteristics, tin has an extended use in the arts. The use of *tin-foil* for wrapping purposes is well known; *tin-plate*† is sheet iron which has been carefully cleaned and coated with tin by immersion in the fused metal; the crystalline structure of such a tin-surface may be exhibited by acting on it for a short time with dilute *aqua regia*, when most beautiful markings are obtained. Copper vessels are tinned inside by rubbing the clean hot surface with molten tin; *pins* are made of tinned brass wire.

The alloys of tin are of great practical importance, owing to their varied and useful properties—*e.g.*, *Britannia metal* (tin and antimony), *pewter* (tin and lead), *solder* (tin and lead), *speculum metal* used for the

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* Under these circumstances ammonia is also formed, and dissolves in the excess of acid, forming ammonium nitrate:—$4\,Sn + 10\,H\,N\,O_3 = 4\,Sn\,(N\,O_3)_2 + N\,H_4\,N\,O_3 + 3\,H_2\,O$.

† In this combination the tin is the negative, the iron the positive metal; in consequence of which, whenever the coating of tin becomes defective, the exposed iron rusts even more quickly than it would do without the tin coating.

mirrors of reflecting telescopes, *bell-metal*, *gun-metal*, and *bronze* (tin and copper), and finally *tin-amalgam* (tin and mercury), used for silvering glass.

Preparation.—The ore, after roasting to free it from sulphur and arsenic, which is present as arsenical pyrites, is reduced by heating with coal, and the reduced metal cast into blocks (*block tin*); *grain tin*, so-called because in fragments, is a purer form of the metal obtained by re-melting and drawing off the upper portion of the metal, which is more free from alloy than the lower portion, and hence more brittle.

OXIDES OF TIN.

Tin forms two oxides only—

Stannous Oxide, . .	$Sn\ O$.
Stannic Oxide, . .	$Sn\ O_2$.

Stannous Oxide (*tin monoxide*), $Sn\ O = 134$.

A dark-brown powder obtained by heating the hydrate in an atmosphere of carbonic anhydride; it remains unchanged in air at ordinary temperatures, but when heated ignites and burns to dioxide.

Stannous Hydrate, $Sn_2\ H_2\ O_3 = 286$. $[2\ Sn\ O\ .\ H_2\ O]$.

This compound is obtained as a white precipitate when a solution of potassium carbonate is added to a solution of stannous chloride ($Sn\ Cl_2$), carbonic acid being at the same time evolved. This hydrate becomes rapidly oxidised in contact with air; it is soluble in caustic potash solution, probably forming *potassium stannite* $[K_2\ Sn_2\ O_3 = K_2\ O\ .\ 2\ Sn\ O]$; the solution on boiling deposits metallic tin, and contains *potassium stannate* ($K_2\ Sn\ O_3$).

Stannous oxide acts also as a basic oxide, forming *stannous salts*, in which the tin plays the part of a dyad.

Stannic Oxide (*tin dioxide*), $Sn\ O_2 = 150$.

Occurrence.—As *tin-stone* or *cassiterite* (see *occurrence* of Tin), of specific gravity, 6·8 to 7, massive, or in dark-brown crystals belonging to the square prismatic system; sulphides and arsenides of copper and iron are usually associated with it.

Properties.—Stannic oxide, artificially produced by igniting the hydrate, is a white powder, turning yellow and brown on heating, but resuming its original colour on cooling. Both the natural and artificial forms are insoluble in water and in acids (except sulphuric), and fusible only at a high temperature. This oxide is an acid-forming oxide, it combines with caustic potash or soda, when fused with them, forming *stannates*, and several salts are known corresponding to its hydrates (*stannic and metastannic acids*), but it also acts as a weak base forming salts called *stannic salts*, in which the tin plays the part of a tetrad.

Preparation.—1. *Amorphous*—By igniting the hydrate produced by the action of strong nitric acid on tin. 2. *Crystalline*—By heating amorphous oxide in a current of hydrochloric acid gas.

Hydrates of Stannic Oxide—Stannic and Metastannic Acids.—The precipitate produced by adding ammonia solution or calcium carbonate to a solution of stannic chloride ($Sn\,Cl_4$, see below) has, after drying *in vacuo*, the composition, $H_2\,Sn\,O_3$ or $Sn\,O_2 \cdot H_2\,O$. This compound is soluble in acids, and is dissolved by caustic potash or soda solutions, forming crystalline compounds on evaporation, of the composition, $M_2\,Sn\,O_3$; this hydrate is known as *stannic acid*, and its salts as *stannates;* an aqueous solution of the sodium salt (*tin-prepare liquor*) is used as a mordant in calico printing.

The hydrate of stannic oxide produced by the action of nitric acid on tin is apparently of more complicated composition, its formula is generally stated to be $H_{10}\,Sn_5\,O_{15}$, or $5\,H_2\,Sn\,O_3$. This hydrate is called *metastannic acid*, and its imperfectly known compounds *metastannates.* It is considered by some chemists to be another form of stannic acid; it is insoluble in acids, but difficultly soluble in solutions of caustic alkalies, and forms salts of complicated composition with the alkali metals, *e.g.*, two sodium salts of the following composition are known: $Na_2\,H_8\,Sn_3\,O_{15}$ or $Na_2\,Sn_5\,O_{11}, 4\,H_2\,O$ and $Na_2\,Sn_9\,O_{19}, 8\,H_2\,O$.

STANNOUS SALTS (Sn'').

Of these salts the chloride is the only important one.

Stannous Chloride (*tin salt*), $Sn\,Cl_2$, $2\,H_2\,O = 189 + 36 = 225$. *Specific gravity, of crystalline*, 2·71 (*water* = 1). *Fusing point of anhydrous*, 249·3°.

Properties.—This salt may be obtained in monoclinic crystals containing two molecules of water, which it loses at 100°; it is soluble in about one-third of its weight of water. If much water is added a basic salt is precipitated—$Sn\,Cl_2 + H_2\,O = Sn\,O\,H\,Cl + H\,Cl$, and if the solution is exposed to the air, the same precipitate and an oxychloride are formed together with stannic chloride—$4\,Sn\,Cl_2 + H_2\,O + O = Sn\,O\,Cl_2 + 2\,Sn\,O\,H\,Cl + Sn\,Cl_4$; the salt has in fact a great tendency to form the tetrachloride; it is converted into tetrachloride by addition of chlorine water, and it acts as a powerful reducing agent owing to this attraction for chlorine—thus, with a solution of mercuric chloride, a solution of stannous chloride gives first a white precipitate ($Hg_2\,Cl_2$), which quickly becomes grey, metallic mercury being precipated:—(*a*) $Sn\,Cl_2 + 2\,Hg\,Cl_2 = Sn\,Cl_4 + Hg_2\,Cl_2$, (*b*) $Sn\,Cl_2 + Hg_2\,Cl_2 = Sn\,Cl_4 + Hg_2$. Cupric chloride ($Cu\,Cl_2$) is similarly reduced to cuprous chloride ($Cu_2\,Cl_2$). Its action on gold chloride ($An\,Cl_3$) producing the precipitate called *purple of Cassius* (see *gold*) is also partly due to reduction. The anhydrous salt ($Sn\,Cl_2$) may be distilled without decomposition.

Preparation.—Metallic tin is easily soluble in hydrochloric acid, and this solution (with excess of tin to reduce any stannic chloride formed) is often used as a reagent; from it, crystals of the composition $Sn\,Cl_2, 2\,H_2\,O$, may be obtained by evaporation. The anhydrous chloride may be obtained by heating the hydrate, or by distilling a mixture of powdered tin and mercurous chloride ($Hg_2\,Cl_2$).

Stannous Sulphate, $Sn\,SO_4$, may be obtained crystalline with difficulty by evaporating *in vacuo* a solution of tin in sulphuric acid.

Stannous Nitrate, $Sn\,(N\,O_3)_2$, is known only in solution; it is prepared by acting on the metal with very dilute nitric acid (see *tin*, p. 298).

Stannous Sulphide (*tin monosulphide*), $Sn\,S = 150$.

The anhydrous sulphide obtained by heating tin and sulphur together is dark-grey in colour, the hydrated form is obtained as a dark-brown precipitate on passing sulphuretted hydrogen through a solution of stannous chloride; it is soluble in polysulphide (yellow sulphide) of ammonium.

STANNIC SALTS (Sn^{iv}).

Stannic Chloride (*tin tetrachloride*, *liquor Libavii fumans*, *butter of tin*, *oxymuriate of tin*), $Sn\,Cl_4 = 260$. *Specific gravity*, 2·25 (*water* = 1). *Boiling point*, 113·9°.

Properties.—This salt in the anhydrous form is at ordinary temperatures a fuming liquid of specific gravity 2·27, and boils at 150°. It forms several hydrates—viz., with 3, 5, and 8 molecules of water—which all crystallise in the monoclinic system, and are soluble in water. With much water it breaks up into hydrochloric acid and stannic acid ($H_2\,Sn\,O_3$), which is precipitated. It is used as a mordant.

Preparation.—By distilling tin with corrosive sublimate ($Hg\,Cl_2$), or by passing a stream of chlorine over fused tin in a retort.

Stannic Sulphate, $Sn\,(S\,O_4)_2$, and **Stannic Nitrate**, $Sn\,(N\,O_3)_4$, are but imperfectly known.

Stannic Sulphide (*tin disulphide*, *Mosaic gold*), $Sn\,S_2 = 182$.

This compound may be obtained in glittering yellow scales by heating a mixture of tin, sulphur, and sal-ammoniac ($N\,H_4\,Cl$), when the disulphide of tin is formed and sublimes; or as a bright-yellow hydrate when sulphuretted hydrogen is passed through a solution of stannic chloride. It is soluble in polysulphides of the alkalies, forming *sulphostannates*, corresponding to sulphostannic acid, $H_2 Sn S_3$, a compound which is also known.

Distinguishing Characters of the Compounds of Tin.—With the exception of the sulphides, the salts of tin are colourless, unless the acid is coloured; they are mostly soluble in water, but many are decomposed by it.

Both stannous and stannic salts give a white precipitate, with *caustic potash* solution (see above), soluble in excess. Stannous salts give a dark-brown precipitate, stannic salts a yellow precipitate, with *hydrogen sulphide* (see above). A solution of *gold chloride* ($Au Cl_3$) gives, with stannous chloride, in presence of a small quantity of stannic chloride, a purple precipitate (purple of Cassius). *Mercuric chloride* gives, with stannous chloride, a white precipitate ($Hg_2 Cl_2$), becoming grey on heating (Hg).

Zinc causes a precipitation of spongy tin in solutions of tin salts.

Physiological Action.—Poisonous.

TITANIUM.[*]

Ti = 48. *Tetrad.*

Occurrence in Nature.—This rare metal does not occur in the free state, but chiefly as dioxide ($Ti O_2$) in the minerals *rutile*, *brookite*, and *anatase;* and as trioxide in *ilmenite* $(Fe Ti)_2 O_3$, &c.; it sometimes accompanies magnetic iron ore, and is consequently found (as nitride and cyanide) in the slag of iron furnaces. It is a constituent, in small quantity, of many minerals.

Properties.—As usually prepared it is a dark grey powder resembling reduced iron; it is specially characterised by its attraction for nitrogen, with which it forms several compounds ($Ti_2 N_2$, $Ti_3 N_2$, $Ti_3 N_4$?) of metallic appearance, which yield ammonia when fused with caustic potash; it combines readily with oxygen, taking fire and burning brilliantly when heated in air, with formation of dioxide and some nitride; it must therefore be prepared out of contact with the atmosphere. It begins to decompose water at 100°. It is soluble in most acids.

Preparation.—By fusing potassium titano-fluoride with metallic sodium in a covered crucible.

Oxides and Salts.—Titanium forms two oxides, $Ti O_2$ and $Ti_2 O_3$, and the dioxide forms hydrates, known as titanic and meta-titanic acids, which are analogous to the corresponding tin compounds. Two chlorides, $Ti Cl_2$ and $Ti Cl_4$ are known, and many other salts.

Distinguishing Tests.—Titanium oxide gives a violet bead with microcosmic salt when heated in the inner flame. Solutions of titanium compounds give with zinc and hydrochloric acid (nascent hydrogen) a violet solution.

THORIUM[†]—Th = 231.

This metal occurs in the very rare minerals *thorite* or *orangite* (a silicate of thorium), and *monazite* (a phosphate of thorium, cerium, &c.). It has an iron-grey colour, specific gravity,

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[*] In classical allusion to *Titan*, a son of the Earth.

[†] In allusion to the Scandinavian deity, *Thor*.

7·8; remains unaltered in air at ordinary temperatures, but when slowly heated burns with brilliancy to dioxide (Th O_2), the only oxide which it is known to form. Several salts have been prepared. The metal is obtained by heating the chloride (Th Cl_4) with sodium. The dioxide has been obtained in prismatic crystals, isomorphous with *cassiterite* (Sn O_2) and *rutile* (Ti O_2).

ZIRCONIUM—Zr = 89·6.

Specific heat, 0·0662.

This metal is found in certain scarce minerals, especially in *zircon* (Zr Si O_4), and has been prepared in the free state as an amorphous powder, by heating the chloride, Zr Cl_4, with sodium, or crystalline by heating potassium zircono-fluoride (K_2 Zr F_6) with aluminium to a very high temperature; when amorphous, it ignites at a comparatively low temperature, but when crystalline only at a very high temperature. It forms a dioxide which possesses both acid and basic properties, and which has also been obtained in prismatic crystals isomorphous with *cassiterite* (Sn O_2) and *rutile* (Ti O_2).

BISMUTH.*

Bi = 210. *Specific gravity*, 9·9. *Melting point*, 268·3°.
Specific heat, 0·0308. *Pentad*.

Occurrence in Nature.—Bismuth is one of the less common elements; it is chiefly found *native*, but also as oxide in *bismuth-ochre* (Bi_2 O_3), and as sulphide in *bismuthite* (Bi_2 S_5); it occurs further in a few rare minerals as carbonate, telluride, vanadate, and silicate.

Properties.—Bismuth is a white metal with a tinge of red. It is permanent in air at ordinary temperatures, but oxidises rapidly at a red heat. It is very brittle, and has a strong tendency to crystallise. It crystallises in rhombohedra, in shape closely approximating to cubes. It melts at a temperature of 263°, and, like water, expands very appreciably on solidifying. It is readily soluble in nitric acid, difficultly soluble in sulphuric acid, and practically insoluble in hydrochloric acid.

The pure metal is not used in the arts, but is frequently employed as an admixture in various alloys, most of which are remarkable for their low melting points. *Rose's metal* is an alloy which melts at 94°, and consists of 2 parts bismuth, 1 part tin, and 1 part lead.

So-called *fusible metal* is an alloy of bismuth, tin, and lead, which, by varying the proportion of the constituents, can be obtained of very varying melting point; use is made of this alloy to prevent explosions in boilers, a plate of the alloy being let into the boiler, so that as soon as the temperature of the steam reaches the melting point of the alloy the plate fuses and allows a vent to the steam, it is thus impossible for the steam to reach a tension beyond that which the boiler is capable of resisting (p 37).

Preparation.—Commercially the metal was formerly prepared by simply heating the crude native ore in inclined iron tubes in suitable

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* German *Wismuth*, from the old German *Wesemoth*, mown grass, *math*, in allusion to the variety of colours seen on the surface of crystallised bismuth, and supposed to resemble mown grass interspersed by flowers.

furnaces, so that the metal melted and flowed down the tube, leaving the matrix or gang behind. Now, generally the ore is first roasted, and afterwards reduced in crucibles by means of carbon.

Commercial bismuth may be purified by fusing it with nitre, but the pure metal is best obtained by heating the basic nitrate with charcoal.

OXIDES OF BISMUTH.

Bismuth yields several compounds with oxygen:—

Bismuthous Oxide, . .	$Bi\ O\ (Bi_2\ O_2)$.
Bismuthic Oxide, . .	$Bi_2\ O_3$.
Bismuthic Anhydride, . .	$Bi_2\ O_5$.

Of these, however, the second one only is of any practical importance.

Bismuthic Oxide, $Bi_2\ O_3 = 468$.

Properties.—A yellowish powder, which melts at a red heat, and on cooling solidifies to a crystalline mass. It is readily soluble in acids yielding salts, in which the double atom is hexad. It is a feebly basic oxide, the normal salts of which are decomposed by water, with the formation of difficultly soluble basic salts.

Preparation.—By heating bismuth in air; by heating the basic nitrate, or by boiling it in caustic soda solution.

Bismuthic Hydrate, $Bi_2\ H_2\ O_4 = 486$. $[Bi_2\ O_3,\ H_2\ O]$.

Properties.—A white powder, readily soluble in acids; on heating it loses water and becomes anhydrous.

Preparation.—By precipitating a solution of a bismuthic salt with caustic soda, and drying the washed precipitate at 100°.

SALTS OF BISMUTH.

Nitrates of Bismuth.—(*a.*) *Normal.*—Metallic bismuth dissolves in nitric acid, with evolution of nitric peroxide, and this solution, on evaporation, yields large, colourless, transparent crystals of the composition, $\mathrm{Bi\ (NO_3)_3,\ 5\ H_2\ O}$. The salt is soluble in a little water without decomposition; but on addition of more water the solution becomes turbid and deposits a white crystalline powder of *basic nitrate*, $\mathrm{Bi_3\ N_3\ H_6\ O_{15} = Bi\ (NO_3)_3,\ Bi_2\ O_3,\ 3\ H_2\ O}$, known in *materia medica* as tris-nitrate or sub-nitrate of bismuth—

$$\mathrm{3\,Bi\,(N\,O_3)_3,\ 5\,H_2\,O + H_2\,O = Bi\,(N\,O_3)_3,\ Bi_2\,O_3,\ 3\,H_2\,O + 6\,H\,N\,O_3}.$$

This compound may also be regarded as the hydrated salt of an *orthonitric acid*, $\mathrm{H_3\ N\ O_4}$ or $\mathrm{H\ N\ O_3,\ H_2\ O}$; in which case its formula would be $\mathrm{Bi\ N\ O_4,\ H_2\ O}$.

Bismuth Chloride, $Bi\,Cl_3 = 316{\cdot}5$.

This salt is formed when bismuth is dissolved in *aqua regia*, or when bismuthic hydrate is dissolved in excess of hydrochloric acid; like the nitrate and other salts, it is decomposed by much water, forming an oxychloride, $Bi\,Cl_3 + H_2\,O = Bi\,O\,Cl + 2\,H\,Cl$.

Characters of Bismuthic Salts.—The normal salts of bismuthic oxide are soluble only in presence of an excess of acid, and are decomposed by water, with formation of difficultly soluble basic salts. The acidified solution of a bismuth salt yields with sulphuretted hydrogen a brown precipitate ($Bi_2\,S_3$), insoluble in sulphide of ammonium; with caustic alkalies and with ammonia, a white precipitate insoluble in excess of the reagent.[*] Heated on charcoal in the reducing flame they yield a brittle metallic bead and a yellow incrustation of oxide.

Physiological Action.—The basic nitrate is used as an external application, as well as internally as a sedative and astringent and as an anti-emetic.

NORWEGIUM.

Ng = 214 (?). *Specific gravity*, 9·441. *Melting point*, 254°.

This rare metal was discovered by Dahl in nickel glance from Kragerö in Norway. It is white, melts at 254°, and readily volatilises before the blowpipe. It yields a brown oxide ($Ng_2\,O_3$?), containing 9·879 per cent. of oxygen, which is readily reduced by fusion with sodium carbonate or potassium cyanide. It colours the borax bead blue.

The metal shows great affinity to bismuth, but differs from this metal in the solubility of its hydrated oxide in a solution of caustic potash, and also in great excess of solutions of ammonium or sodium carbonate.

ANTIMONY.[†]

(*Antimonium, stibium*), *Sb* = 122. *Specific gravity, amorphous*, 5·78; *crystalline*, 6·7 (*water* = 1). *Specific heat*, 0·0508. *Melting point*, 432°. *Boiling point, between* 1090° *and* 1450. *Triad to pentad.*

Occurrence in Nature.—Antimony is rarely found native; its most common occurrence is as trisulphide in *stibnite*, $Sb_2\,S_3$; it is found also as trisulphide in combination with sulphides of lead, mercury, copper,

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[*] In presence of tartaric or citric acids the precipitate produced by caustic alkalies or their carbonates, or by ammonia or carbonate of ammonia, redissolves on addition of an excess of the reagent.

[†] The origin of this name appears to be lost; Basilius Valentinus (15th century), in speaking of the common ore of antimony, the sulphide (stibnite), says that the Arabians called it *asinat*, the Chaldeans, *stibium*, and that "in the Latin tongue it has hitherto been termed *antimonium*."—*Vide* Kopp, *Geschichte der Chemie*, vol. iv. Probably both *antimonium* and *stibium* are alchemistic corruptions of the Arabic name *uthmud* (*othmod, ithmid*).—*Vide* Murray, *New English Dict.*, 1885, Pt. ii., p. 370.

silver, &c., these minerals having the general formula, M S, $Sb_2 S_3$ (sulphantimonites); it is found also in direct combination with some metals as in *antimonial silver*, $Ag_2 Sb$, *antimonial nickel*, Ni Sb, *arseniferous antimony*, $As_3 Sb_2$; it is also found as trioxide, $Sb_2 O_3$, and as tetroxide, $Sb_2 O_4$.

Properties.—Antimony is a bluish-white metal; it is extremely brittle, and can easily be reduced to powder; it has a marked crystalline structure, and may be obtained in rhombohedral crystals. It melts at 432°, and volatilises only at a bright red heat; if a portion of the molten metal is poured upon a hard surface it splits up into a number of globules, which ignite and are scattered in every direction, leaving a number of white streaks of oxide radiating from the central point. The metal, contrary to the usual rule, expands on solidifying. When very strongly heated in contact with air, it ignites and burns to trioxide or tetroxide. At ordinary temperatures it remains unaltered in air.

It is soluble in hot concentrated hydrochloric acid, with evolution of hydrogen and formation of the trichloride ($Sb Cl_3$), and in *aqua regia*, with formation of the trichloride or of the pentachloride ($Sb Cl_5$), according to the quantity of the solvent. Heated with strong sulphuric acid, sulphurous anhydride is evolved and antimony trisulphate [$Sb_2 (SO_4)_3$] formed. Nitric acid oxidises it to antimonic acid ($Sb_2 O_5 . H_2 O$), a white insoluble powder.

Antimony forms a number of important alloys, among which may be mentioned *type-metal* (2 lead, 1 antimony, and 1 tin), to which it imparts the property of expanding on solidifying, so that a sharp casting is obtained, and *Britannia metal* and *pewter* (tin and antimony).

It forms two series of compounds—viz., antimonious, in which it plays the part of a triad; and antimonic, in which it plays the part of a pentad element.

Preparation.—1. By heating the fused sulphide with scrap iron, $Sb_2 S_3 + 3 Fe = 3 Fe S + Sb_2$. 2. By heating the oxide (obtained by careful roasting of the sulphide) with charcoal. 3. By fusion of the sulphide with sodium carbonate and charcoal—(*a*) $Sb_2 S_3 + 3 Na_2 CO_3 = 3 CO_2 + 3 Na_2 S + Sb_2 O_3$; (*b*) $Sb_2 O_3 + 3 C = 3 CO + Sb_2$.

The commercial product is liable to contain arsenic, lead, copper, and iron.

A remarkable amorphous modification may be obtained by the electrolysis of a solution of tartar emetic in antimonious chloride. It has a specific gravity of 5·78, a steel-grey colour, and is somewhat unstable, changing when heated, or struck, into ordinary antimony with considerable rise in temperature.

Antimoniuretted Hydrogen (*antimony hydride, Stibine*), $Sb\ H_3 = 125$.

Properties.—This gas has not been obtained pure, but is always, owing to its method of preparation, mixed with hydrogen. This mixture burns with a white flame, which deposits metallic antimony upon a porcelain surface brought into contact with it, or if a glass-tube through which the gas is passing is locally heated by the flame of a Bunsen burner, a deposit of antimony (antimony mirror) is formed on both sides of the flame. Passed into a solution of silver nitrate, it causes a black precipitate, having the composition, $Ag_3\ Sb$.

Antimoniuretted hydrogen behaves in a distinctly analogous manner to the corresponding compound of arsenic, but may nevertheless be easily distinguished from that compound; the antimony mirror is deposited nearer the flame and on both sides of it, the metal being less volatile than arsenic; the antimony deposits are insoluble in sodium hypochlorite, and yield an orange colour on evaporation, with a drop of ammonium sulphide (*cf.*, arsenic, p. 315); the action of the two compounds on silver nitrate solution is also very different, and may even be employed for their separation (*cf.*, arsenic). Further, the antimony compound is odourless.

Preparation.—By placing a solution of an antimony compound in an apparatus in which hydrogen is being generated; generally by pouring a solution of the trichloride into a Woulff's bottle containing zinc and dilute sulphuric acid; whereupon antimoniuretted hydrogen is formed, and escapes with the hydrogen.

OXIDES OF ANTIMONY.

Antimony Trioxide, $Sb_2\ O_3 = 292$. *Specific gravity,* 5·2 *to* 5·5 (*water* = 1).

Occurrence.—This oxide is dimorphous, and occurs but rarely n *valentinite*, or *white antimony*, in right prismatic crystals, and in *senarmontite* in regular octahedra.

Properties.—This oxide may be obtained artificially in the forms in which it occurs in nature, or as a pale buff-coloured crystalline powder, which melts at a red heat, and solidifies on cooling to a crystalline mass. It is only very slightly soluble in water, and is insoluble in nitric acid and in dilute sulphuric, but soluble n hydrochloric acid, forming the trichloride, and in a solution of tartaric acid forming the tartrate; it is also dissolved by a solution of acid potassium, tartrate, or *cream of tartar* ($K\ H\ C_4\ H_4\ O_6$), forming a compound known as *tartar emetic* [$K\ (Sb\ O)\ C_4\ H_4\ O_6$], in which the monatomic radical *antimonyl* ($Sb\ O$) is substituted for the remaining replaceable hydrogen atom of the acid tartrate.

Heated without access of air it sublimes and condenses in acicular crystals; heated in air it burns, forming a higher oxide.

Antimony trioxide possesses weak acid characters; it dissolves in solutions of caustic alkalies, forming unstable salts called *antimonites*, which have the general formula, $M\,Sb\,O_2$, and which are referable to a hydrate, viz., antimonious acid, $Sb\,O\,(O\,H)$, or $Sb_2\,O_3 \,.\, H_2\,O$. A hydrate of this composition has been obtained.

Preparation.—1. By burning antimony, with limited access of air. 2. By carefully roasting antimony trisulphide. 3. By pouring an acid solution of the chloride into water, digesting the basic salt so produced with sodium carbonate, and finally heating the resulting hydrate till it is anhydrous.

Antimony Tetroxide (*antimonious-antimonic oxide*), $Sb_2\,O_4 = 304$. $[Sb_2\,O_3 \,.\, Sb_2\,O_5]$.

Occurrence.—As the mineral *cervantite.*

Properties.—This oxide, which is a grey infusible powder, insoluble in water, and difficultly soluble in acids, is regarded by some as a mixture of trioxide and pentoxide, and most of its compounds are referable to such a composition. It has weak acid characters, and forms salts with the alkalies, having the general formula, $M_2\,O \,.\, Sb_2\,O_4$, they are called *hypo-antimoniates* (often also *antimonites*), and are possibly mixtures of antimonites and antimonates.

Preparation.—1. By oxidation of the trioxide by heating it in air. 2. By deoxidation of the pentoxide by heating it in air.

Antimony Pentoxide, $Sb_2\,O_5 = 324$. *Specific gravity*, 5·6 (*water* = 1).

Properties.—A light-yellow powder, almost insoluble in water, slowly soluble in hydrochloric acid, insoluble in nitric acid. On heating, it loses oxygen, and is converted into tetroxide.

It forms two hydrates, *antimonic acid*, $H\,Sb\,O_3$ or $Sb_2\,O_5$, $H_2\,O$, and *metantimonic acid*, $H_4\,Sb_2\,O_7$ or $Sb_2\,O_5 \,.\, 2\,H_2\,O$, which, on account of their analogy to the corresponding phosphoric acids, would be more properly termed metantimonic and pyrantimonic acids respectively. These acids form definite salts known as *antimoniates* and *metantimoniates* respectively; the acid potassium metantimoniate ($K_2\,H_2\,Sb_2\,O_7$), is used in the laboratory as a reagent for the detection of sodium, which it precipitates from comparatively dilute solutions in the form of acid sodium metantimoniate ($Na_2\,H_2\,Sb_2\,O_7$).

Preparation.—The hydrates are formed when antimony is acted on with excess of nitric acid; the anhydrous oxide by gently heating the hydrates; *potassium antimoniate* ($K\,Sb\,O_3$) may be prepared by fusing metallic antimony with nitre; *normal potassium metantimoniate* ($K_4\,Sb_2\,O_7$)

is formed when the antimoniate is fused with caustic potash, and the fused mass dissolved in water and the solution evaporated to crystallisation, the deliquescent crystals so obtained are decomposed by a small quantity of water forming the *acid metantimoniate*, $K_2 H_2 Sb_2 O_7$.

Antimony Sulphate (*antimonious sulphate, antimony trisulphate*), $Sb_2 (S O_4)_3 = 532$. This salt may be obtained in silky needles from an acid solution of the trioxide in strong sulphuric acid. It is decomposed by water with formation of a soluble acid salt, and an insoluble basic salt.

Antimony Trisulphide (*antimonious sulphide, kermes-mineral*), $Sb_2 S_3 = 340$. *Specific gravity*, 4·62.

Occurrence.—This compound occurs in comparative abundance, and is somewhat widely diffused as the mineral *stibnite*, crystallised in rhombic prisms, or in columnar masses, sometimes of considerable size. Combined with other sulphides, it forms a great number of minerals, which may be regarded as sulphosalts, or sulphantimonites (see Antimony, p. 305).

Properties.—The naturally occurring sulphide is grey and very brittle, the precipitated sulphide has a fine orange colour, and this, when strongly heated, becomes permanently grey like the mineral. It is dissolved by a solution of caustic potash on warming, forming the trioxide ($Sb_2 O_3$), which separates out in a crystalline form, and potassium sulphantimonite ($K_2 S, Sb_2 S_3$); this latter compound induces a further solution of the trisulphide, which is again deposited on cooling the solution, but the sulphide so precipitated is usually mixed with oxide and some potassium sulphide; it was this somewhat impure amorphous trisulphide which constituted the *kermes-mineral** of the alchemists, a preparation much valued by them as a medicine.

Antimony sulphide is also soluble in solutions of the alkaline sulphides.

Preparation.—1. By precipitating a solution of *tartar emetic* [$K (Sb O) C_4 H_4 O_6$] with hydrogen sulphide, a slightly hydrated amorphous orange precipitate is produced, which, on gently heating, darkens in colour, becoming anhydrous, but on strongly heating becomes permanently grey and crystalline. 2. By fusing antimony with sulphur.

Uses.—It is largely employed for vulcanising caoutchouc.

Antimony Pentasulphide (*antimonic sulphide, sulphur auratum*), $Sb_2 S_5 = 404$.

Properties.—A yellowish-red powder, which, like the trisulphide, is soluble in solutions of the alkaline sulphides, forming *sulphantimonates;*

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* So called from its resemblance in colour to the cochineal insect, kermes.

sodium sulphantimonate, $Na_3 Sb S_4$ or $3 Na_2 S . Sb_2 S_5$, may be obtained in large crystals; and several other salts are known.

Preparation.—By addition of dilute sulphuric acid to a solution of sodium sulphantimonate; this latter is prepared by boiling with water a mixture of the trisulphide of antimony, sodium carbonate, slaked lime, and sulphur, filtering and evaporating to crystallisation.

Antimony Trichloride (*butter of antimony*), $Sb Cl_3 = 228{\cdot}5$. *Specific gravity*, 2·67 (*water* = 1). *Melting point*, 73·2°. *Boiling point*, 223·5°.

Properties.—A colourless crystalline compound, which is excessively deliquescent and soluble in water containing not less than 15 per cent. of hydrochloric acid. The solution on mixing with water yields a white precipitate of the basic chloride ($Sb O Cl$). This compound, formerly employed as a medicine, was called *Powder of Algaroth.*[*]

Preparation.—1. By distilling antimony or antimony trisulphide with mercuric chloride ($Hg Cl_2$). 2. A strong solution may be obtained by dissolving the trisulphide in hydrochloric acid. 3. The trichloride is formed when powdered antimony is thrown into chlorine gas.

Uses.—The brown surface on steel in guns, &c., is produced by means of antimony trichloride.

Antimony Pentachloride, $Sb Cl_5 = 297{\cdot}5$. *Specific gravity*, 2·34 (*water* = 1). *Melting point*, − 6°.

A white fuming liquid, decomposed by water, with formation of basic chlorides or metantimonic acid and hydrochloric acid. It is prepared by saturating the trichloride with chlorine. Decomposed by heating into antimonious chloride and free chlorine.

General Characters of Compounds of Antimony.—Most of the compounds of antimony, except *tartar emetic* [$K (Sb O) C_4 H_4 O_6$], are insoluble or difficultly soluble in water; many are soluble in dilute or strong hydrochloric acid.

Acid solutions of antimony salts yield, with *hydrogen sulphide*, a characteristic orange-red precipitate of the trisulphide ($Sb_2 S_3$), soluble in a solution of potash or of ammonium sulphide, insoluble in ammonium carbonate solution (distinction from arsenic) and in dilute hydrochloric acid; solutions of caustic potash or soda, or potassium carbonates, precipitate hydrated oxide [$Sb O (O H)$], soluble in tartaric acid; zinc, iron, and copper produce a black precipitate of metallic antimony; in contact with nascent hydrogen they form antimoniuretted hydrogen, which may be specially recognised (see p. 307).

Heated on charcoal with sodium carbonate antimony compounds

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[*] After Algarotus, a Veronese physician.

yield a white brittle metallic globule and a white incrustation of trioxide.

Physiological Action.—Compounds of antimony act as irritant poisons in large doses, or may prove fatal in small repeated doses, owing to their depressing effect on the heart's action. They are used medicinally on account of their counter-irritant, emetic, sedative, expectorant, &c., action.

ARSENIC.

(*Latin*, *arsenicum*; *Greek*, ἀρσενικόν*). $As = 75$; $As_4 = 300$. *Specific gravity*, *of solid*, 5·7 *to* 5·9 (*water* $= 1$); *of vapour*, 150 ($H = 1$). *Specific heat*, 0·0814. *Volatilises at about* 180°; *melts under pressure at about* 500°.

Occurrence in Nature.—Arsenic is found very widely distributed, and is sometimes found native; its chief occurrence is as an arsenical sulphide of iron in the mineral *mispickel* ($Fe\,As\,S$); it is also found as disulphide in *realgar* (As_2S_2), and as trisulphide in *orpiment* (As_2S_3), and in numerous other minerals in direct combination (arsenides) with iron, nickel, cobalt, tin, copper, antimony, &c. In traces it is found in iron pyrites, in soils, in some mineral waters, &c.; it is present in commercial sulphuric acid made from pyrites, and in almost all commercial zinc.

Properties.—Arsenic is of a steel-grey colour, and possesses a marked metallic lustre; it is highly crystalline in structure, very brittle, and easily powdered. Heated to about 180° it volatilises without fusion; its vapour density compared to hydrogen is, contrary to the usual rule, twice as great as its atomic weight, and its molecule is therefore assumed to contain four atoms instead of two (*cf.*, p. 61). The vapour is colourless, and has a peculiar garlic-like odour. If the metal is heated with access of air it takes fire and burns to the trioxide, As_2O_3. Exposed to dry air it remains unaltered, but if moist it becomes partially oxidised.

Hydrochloric acid has very little action upon it; nitric acid and *aqua regia* convert it into arsenic acid (As_2O_5, $3\,H_2O$; H_3AsO_4).

Preparation.—*From mispickel* ($Fe\,As\,S$).—The ore is roasted, and the fumes which mainly consist of arsenious oxide (As_2O_3) are condensed

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* The name ἀρσενικόν was used by Theophrastos, a pupil of Aristotle, in the fourth century, B.C., to denote both *realgar* (As_2S_2) and *orpiment* (As_2S_3), then considered to be identical; this name was adopted by the alchemists of the fifteenth century, and was by them apparently intended to imply that these substances were *male principles* (ἄρσην, a male), in accordance with the ideas prevalent at that period.—See *Kopp.*, *Geschichte der Chemie*, vol. iv.

in special chambers, which, on account of the poisonous nature of this material, are only opened from time to time. The crude oxide so obtained is purified by sublimation, and finally mixed with charcoal and heated to redness in covered crucibles. The reduced metal sublimes, and is condensed in the upper part of the apparatus.

Uses.—Arsenic is added in small quantity to lead used for the manufacture of small shot, as the shot is more readily obtained spherical with this addition.

Arsenious Oxide (*arsenious anhydride*, *trioxide*, *sesquioxide; white arsenic*) $As_2 O_3 = 198$. *Specific gravity, of amorphous variety*, 3·738 ; *of octahedral*, 3·689 (*water* = 1); *of vapour* 198 · 8 (H=1) [$As_4 O_6$?].

Occurrence.—Very rarely found in nature.

Properties.—Arsenious anhydride is usually white and opaque, but is sometimes colourless and transparent; it has a sweetish, astringent taste. On heating it sublimes without fusion, but if rapidly heated it may be fused.

Arsenious anhydride is dimorphous, and isodimorphous with antimonious anhydride ; when sublimed it crystallises in regular octahedra, but sometimes in rhombic prisms ; octahedra are deposited from its aqueous and hydrochloric acid solutions.

An amorphous (*vitreous*) modification is obtained by fusion ; it is glassy and transparent, but gradually becomes white, opaque, and crystalline (*porcelain variety*), at the same time becoming less soluble in water. The crystalline variety requires about 80 parts of water, the amorphous variety about 25 parts for solution. At the boiling temperature the crystalline variety is gradually transformed into the amorphous variety, but at ordinary temperature the amorphous is transformed into the crystalline; hence a solution saturated at the boiling temperature gradually deposits crystals (octahedra) of arsenious acid on standing.*

This oxide is easily soluble in hydrochloric acid on heating. Nitric acid converts it into arsenic acid. It is an acid-forming oxide, and many salts are known which correspond to the hydrate, $As_2 O_3 . 3 H_2 O$, or $H_3 As O_3$, called *arsenious acid*, but not known in the free state, although it is probably contained in an aqueous solution of the anhydride. The aqueous solution has an acid reaction.

Physiological Action.—It is a deadly poison.† It exerts a specific inflam-

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* These facts account for the very varied statements made with respect to the solubility of arsenious anhydride in water.

† The best antidote for poisoning by arsenious anhydride is freshly precipitated ferric hydrate ($Fe_2 O_3 . 3 H_2 O$), which forms with it an insoluble compound.

matory action on the stomach in whatever way it may be introduced into the system. In small doses it acts as a tonic and alterative.

Preparation.—By resubliming crude arsenious anhydride, as obtained in the roasting of *mispickel* (see above).

Arsenites.—Arsenious anhydride is soluble in solutions of the caustic alkalies, with formation of somewhat unstable soluble compounds which absorb oxygen from the air, and are decomposed by carbonic anhydride. A very large series of arsenites of various metals are known; they mostly correspond to the hydrate, $H_3 As O_3$, but sometimes to the hydrate, $H As O_2$, and are mostly insoluble in water. The copper salt, $Cu H As O_3$, called *Scheele's green*, is a well-known pigment; the silver salt, $Ag_3 As O_3$, is of a pale-yellow colour.

Arsenic Anhydride (*arsenic oxide*, *arsenic pentoxide*), $As_2 O_5 = 230$.

Properties.—Arsenic anhydride is a white amorphous, rather deliquescent, substance, which dissolves slowly in water, forming arsenic acid, $H_3 As O_4$. On heating it gives up oxygen, and is converted into the trioxide.

Preparation.—(1) By the action of nitric acid or of *aqua regia* on arsenious oxide, evaporating to dryness the solution of arsenic acid so obtained, and heating the residue to a low red heat; (2) or by similar treatment of the solution of arsenic acid obtained by passing chlorine gas into an aqueous solution of arsenious oxide.

Arsenic Acid, $H_3 As O_4 = 162$.

This compound may be obtained in colourless crystals, having the composition $2 H_3 As O_4 . H_2 O$, which lose their water at 100°, and on heating to a higher temperature are converted into *pyro-arsenic acid*, $H_4 As_2 O_7$, and *meta-arsenic acid*, $H As O_3$, respectively, which, on solution in water, are again converted into the normal or *ortho-arsenic acid*, $H_3 As O_4$. This substance is in fact a definite acid, and is analogous to phosphoric acid, forming salts called *arsenates* or *arseniates*, which are in many cases isomorphous with the corresponding phosphates.

Arsenates.—The most common arsenate is the commercial arsenate of soda or disodic hydric arsenate, $Na_2 H As O_4$, isomorphous, with the corresponding phosphate; a large series of arsenates have been prepared, all more or less analogous to corresponding phosphates; the silver salt, $Ag_3 As O_4$, is of a brick-red colour, and is formed when a solution of argentic nitrate is added to a solution of an arsenate; it is soluble in excess of nitric acid or of ammonia. The arsenates of the alkali metals are soluble in water; the rest are insoluble, but are easily dissolved by acids.

Arsenic Disulphide (*Realgar*[*]), $As_2\,S_2 = 215$.

This substance is found in nature in ruby-red monoclinic crystals of specific gravity, 3·5. It may be artificially prepared by fusing a mixture of arsenic and sulphur in the requisite proportions, and so prepared is a transparent ruby-red crystalline mass. It has been used as a pigment, and is a constituent of the so-called *white Indian fire* of pyrotechny.

Arsenic Trisulphide (*auripigment*, *orpiment*[†]), $As_2\,S_3 = 246$.

Occurrence.—This substance is found in nature, sometimes massive, sometimes in transparent yellow monoclinic crystals.

Properties.—Artificially prepared, it is of a fine pale-yellow colour; it becomes darker on heating, melts, and may be distilled; when heated in air it ignites and burns with a pale-blue flame; it is soluble in solutions of the caustic alkalies, and forms a series of sulpho-salts termed *sulpharsenites*, corresponding to the arsenites in composition—*e.g.*, potassium sulpharsenite, $K_3\,As\,S_3$.

Arsenic trisulphide is also dissolved by a solution of ammonium carbonate (distinction from corresponding antimony and tin sulphides). It is insoluble in water and in dilute acids.

Preparation.—1. By fusing sulphur with arsenic in the requisite proportions. 2. By precipitation from a solution of arsenious acid with sulphuretted hydrogen.

Arsenic Pentasulphide, $As_2\,S_5 = 310$.

Properties.—A light yellow, easily fusible substance, which on heating, without access of air, is volatile, without decomposition.

By dissolving the pentasulphide in solutions of caustic alkalies, and by various other means, *sulpharsenates* are formed.

Preparation.—1. By fusing arsenic trisulphide with the requisite proportion of sulphur. 2. By acting on a dilute solution of sodium sulpharsenate with hydrochloric acid—$2\,Na_3\,As\,S_4 + 6\,H\,Cl = 6\,Na\,Cl + 3\,H_2\,S + As_2\,S_5$.

Arsenic Trichloride, $As\,Cl_3 = 181{\cdot}5$.

Properties.—An oily, fuming, colourless liquid, of specific gravity 2·2, which boils at 134°; soluble in strong hydrochloric acid. In contact with water it is decomposed, forming arsenious oxide and hydrochloric acid—$2\,As\,Cl_3 + 3\,H_2\,O = 6\,H\,Cl + As_2\,O_3$. It is highly poisonous. It is formed when arsenic is thrown into chlorine.

Preparation.—1. By passing dry chlorine over arsenic in a retort, and purifying by distillation. 2. By distillation of a mixture of mercuric

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[*] Spanish, *rajalgar;* Arabian, *rahj al-ghar*—powder of the mine, mineral powder.—*Skeat.*

[†] French, *orpiment:* derived from Latin, *auripigmentum*—gold paint.

chloride ($HgCl_2$) and arsenic. 3. By distilling arsenious acid with concentrated hydrochloric acid.

Arseniuretted Hydrogen (*Arsenic trihydride, arsine*), $AsH_3 = 78$. *Gas at ordinary temperatures. Specific gravity*, 2·695 (*air* = 1); 39 (*H* = 1). *Fluid at* – 40°.

Properties.—Arseniuretted hydrogen is a colourless gas of repulsive, garlic-like odour, and acts as a most virulent poison when inhaled, so that the most stringent precautions are necessary in experimenting with it, especially if the gas be pure, and in all cases the experiment should be so conducted that the gas is carried off as fast as formed.

It is usually obtained mixed with hydrogen; the gas is inflammable and imparts to the hydrogen flame a livid blue coloration. If a porcelain surface is held in the flame, a bright black spot of metallic arsenic is formed upon it, and if a glass tube, through which the gas is passing, be locally heated by the flame of a Bunsen burner a brilliant mirror is formed a short space in front of the heated part, in the direction of the issuing gas (*Marsh's test*). If the tube containing such a mirror be heated with access of air, arsenious oxide is formed, and is deposited in the cooler portions of the tube in minute octahedra.

The arsenic spots on porcelain are soluble in a solution of sodium hypochlorite, and yield a pale-yellow mass when a drop of ammonium sulphide is carefully evaporated in contact with them.

Arseniuretted hydrogen reduces many metallic solutions, and when passed into a solution of silver nitrate causes a black precipitate of metallic silver, arsenious acid (which goes into solution) and nitric acid being simultaneously formed (*Hoffmann's test*)—$AsH_3 + 6\,AgNO_3 + 3\,H_2O = 6\,HNO_3 + H_3AsO_3 + 3\,Ag_2$ (*cf.* antimoniuretted hydrogen, p. 307).

Arseniuretted hydrogen is also obtained when a solution of arsenious anhydride is introduced into a boiling solution of caustic potash containing fragments of zinc or aluminium (*Fleitmann's test*); antimony compounds do not yield this reaction.

Preparation.—1. Pure arseniuretted hydrogen may be prepared by acting on zinc arsenide, Zn_3As_2, with hydrochloric acid with the strict precautions above insisted upon. The arsenide of zinc is made by fusing zinc and arsenic together in the requisite proportions. 2. The more common method is to introduce into a Woulff's bottle containing zinc and hydrochloric acid a solution of arsenious acid, whereupon arseniuretted hydrogen is formed and escapes with the hydrogen.

Characters of the Compounds of Arsenic.—The compounds of arsenic are mostly colourless, but some possess a very characteristic colour;

they are not very soluble in water, with the exception of the arsenites and arsenates of the alkali metals.

Solutions of compounds of arsenic, when acidified with hydrochloric acid, give (either at once or on long boiling) a yellow precipitate ($As_2 S_3$) with *hydrogen sulphide;* a grey deposit of metallic arsenic on bright slips of pure copper foil, and this, on heating in contact with air, yields a white sublimate ($As_2 O_3$) of octahedral crystals (*Reinsch's test*); in contact with nascent hydrogen they give arseniuretted hydrogen gas, easily recognised by its highly characteristic properties (see above).

Compounds of arsenic heated with sodium carbonate on charcoal, by means of the blowpipe, emit a peculiar garlic odour; and heated in a glass tube, closed at one end, with potassium cyanide and sodium carbonate yield a bright black sublimate of metallic arsenic.

Arsenates in solution give a brown precipitate ($Ag_3 As O_4$) with silver nitrate solution, soluble in excess of nitric acid or of ammonia; and, on boiling, a yellow precipitate with ammonium molybdate (distinctions from phosphates); and on long boiling with hydrochloric acid yield a yellow precipitate ($As_2 S_3$) with hydrogen sulphide.

Arsenites in solution give a yellow precipitate ($As_2 S_3$) with hydrogen sulphide in presence of hydrochloric acid; a yellow precipitate ($Ag_3 As O_3$) with nitrate of silver solution, soluble in excess of nitric acid or ammonia; and a green precipitate with solutions of copper salts.

Physiological Action.—See Arsenious Acid, p. 315.

VANADIUM.*

$V = 51{\cdot}3$. *Specific gravity*, 5·5 (*water* = 1).

Occurrence in Nature.—This element occurs only in combination in a few rare minerals and chiefly as vanadate—*e.g*, in *vanadinite* [$3\,Pb_3 (VO_4)_2 + Pb\,Cl_2$]; *descloizite*, $Pb_2 V_2 O_7$; *pucherite*, $Bi\,V\,O_4$: *volborthite*, [$(Cu\,Ca)_3 (V\,O_4)_2,\ H_2O$]: *roscoelite*, $4\ Al\,V\,O_4,\ K_4 Si_9 O_{20},\ H_2O$]; *moltramite*, [$(Pb\,Cu)_3 (V\,O_4)_2,\ 2\,Pb\,Cu\,(O\,H)_2$], &c. This last mineral is now its chief source. Traces of vanadium have been found in some clays and iron ores.

Properties—Reduced vanadium is a light whitish-grey coloured powder; it oxidises slowly in air, but takes fire at a high temperature; it does not decompose water at ordinary temperatures; it is soluble in strong sulphuric acid; it absorbs both oxygen and nitrogen, and has to be prepared in an atmosphere of dry hydrogen with the most rigid exclusion of air or moisture.

Preparation.—By heating the dichloride for many hours to a red heat in an atmosphere of dry hydrogen, air being rigidly excluded.

Oxides and Salts.—Vanadium forms five oxides, $V_2 O$, $V_2 O_2$, $V_2 O_3$, $V_2 O_4$, $V_2 O_5$, of which the three first are basic-, the three last, acid-forming. The *vanadates* are referable to a hydrate, $V_2 O_5 . H_2 O$ or $H\,V\,O_3$ (metavanadic), acid, or to orthovanadic acid, $H_3 V\,O_4$, or to pyrovanadic acid, $H_2 V_2 O_7$, but still more complicated salts are known. Chlorides,

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* In allusion to the Scandinavian deity, Vanadis or Freia.

sulphides, sulphates, &c., of vanadium have also been prepared, and others known as vanadyl salts, in which the radical VO is present.

Distinguishing Characters and Tests.—Many vanadium compounds are coloured; hypovanadic sulphate gives a blue solution resembling cupric su'phate, but is not rendered colourless by iron; some vanadates resemble chromates in solution but are rendered blue by deoxidation, not green. Zinc and sulphuric acid (nascent hydrogen) produce a blue coloration in solutions of vanadium compounds.

A solution of vanadic acid, or an acid solution of an alkaline vanadate, becomes red on shaking up with ether and peroxide of hydrogen, even in a solution containing only 1 part of vanadic acid in 40,000 parts of the solution.

NIOBIUM AND TANTALUM.*

$Nb = 94$. $Ta = 182$.

Occurrence in Nature.—These very rare metals occur intimately associated with one another as pentoxides (Ni_2O_5, Ta_2O_5), together with numerous other oxides of iron, manganese, tin, lead, magnesium, calcium, cerium, erbium, yttrium, tungsten, uranium, zirconium, &c., in the minerals *tantalite*, *columbite*, *yttrotantalite*, *fergusonite*, &c.

Properties.—Pure *tantalum* has not been prepared. Roscoe obtained pure *niobium* as a steel-grey crust, by reducing the chloride in hydrogen under special conditions. He estimates its specific gravity at 4·06. It takes fire in air at a low temperature; it appears to be soluble only in strong sulphuric acid.

Oxides and Salts.—The two elements are analogous in every respect; they form oxides of the formula M_2O_4 and M_2O_5, the last forming a hydrate (niobic and tantalic acids), to which the alkaline salts, $M_2Nb_6O_{19}$ or $M_2Ta_6O_{19}$, known as *niobates* and *tantalates* respectively, are referable. They form also analogous chlorides, &c.

Their separation depends upon the greater solubility, in hydrofluoric acid, of potassium niobiofluoride, K_2NbF_6, as compared with potassium tantalofluoride, K_2TaF_6.

Distinguishing Tests.—Solutions of *tantalates* give with potassium ferrocyanide a characteristic yellow precipitate, and tantalum compounds yield no coloured beads with borax or microcosmic salt. Solutions of *niobates* yield with potassium ferrocyanide a brown precipitate, and give a blue coloration with zinc and hydrochloric acid (nascent hydrogen). Niobium compounds colour borax or microcosmic salt, in the reducing flame violet or brown, and red in presence of iron.

COPPER.†

Cu = 63·5. *Specific gravity*, 8·92 *to* 8·95 (*water* = 1). *Specific heat*, 0·0935. *Melting point about* 1,200°. *Volatilises at a white heat. Dyad.*

Occurrence in Nature.—Copper is, comparatively speaking, an abundant element; it is found *native*, sometimes in considerable masses, more particularly in Australia and North America (Lake Superior); it is largely found as sulphide in *copper pyrites* ($CuFeS_2$), as oxide in *cuprite* or *red copper ore* (Cu_2O), and in *tenorite* or *black copper ore* (CuO), as carbonate in *malachite* or *green carbonate of copper* [$CuCO_3$, $Cu(OH)_2$], and *azurite* or *blue carbonate of copper* [$2CuCO_3$, $Cu(OH)_2$], and in innumerable minerals in combination with selenium, arsenic, antimony, and with sulphuric, phosphoric, arsenic, vanadic, and

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* Fanciful names of c'assical origin.

† Formerly known as *Æs Cyprium*, hence cuprum.

silicic acids. In traces, it is very widely diffused in almost all vegetable and animal substances, and in notable quantity in the red colouring-matter of the feathers of certain birds.

Properties.—Copper is the most markedly coloured of all metals, having a peculiar red tint, from which the term *copper-coloured* is derived. It crystallises in the regular system. It is extremely malleable and ductile, can be beaten out into leaves so thin that they transmit light which is of a blue or pink tint. It is the best conductor of heat and electricity after silver. When in the melted state it absorbs various gases, such as carbonic oxide, which, escaping when the metal solidifies, render the mass porous; hence, pure copper is unsuitable for castings. Finely divided copper absorbs up to 0·6 volume of hydrogen. The metal is at ordinary temperatures permanent in dry or even in moist air if all acid be absent, but in presence of any acid it tarnishes very soon. It oxidises rapidly at a red heat. It dissolves slowly in boiling hydrochloric acid with evolution of hydrogen and formation of cuprous chloride, but readily at ordinary temperatures in presence of air; it is soluble in hot, strong sulphuric acid with evolution of sulphurous acid, and in nitric acid with evolution of nitric oxide, in both cases chiefly with production of a cupric salt. In presence of air the metal readily dissolves in ammonia, yielding a deep-blue solution.

Copper is used largely as metal in wire, sheeting, tubing, &c., or in any form which does not require casting. It is also largely used as an alloy with other metals. Thus *brass* consists of 2 parts copper and 1 part zinc; *dutch-metal* of 5 to 6 parts copper and 1 part zinc; *bell-metal* of 4 to 5 parts copper and 1 part tin; *gun-metal* of 9 parts copper and 1 part tin. Our *bronze coinage* contains 95 parts copper, 4 parts tin and 1 part zinc. *Aluminium bronze* contains 90 to 95 parts copper, and 10 to 5 parts of aluminium. An alloy of aluminium consisting of 97 parts of aluminium and 3 parts of copper is whiter than aluminium itself.

Preparation.—1. From the oxide or carbonate by reduction with carbon at a high temperature, and the addition of a slag. 2. From pyrites by alternate roasting in air, and melting out of contact with air, with or without the addition of carbon, and of a suitable slag. During the roasting the sulphides are partially oxidised, sulphurous acid escaping. During the melting the oxide of copper formed during the roasting reacts on the sulphide of iron still present, sulphide of copper is reformed, and oxide of iron produced, which is removed in the slag. In this way the iron is gradually removed and a more or less pure copper sulphide, known as *fine metal*, is obtained. This *fine metal* is once again roasted and melted, generally with the addition of some coal, metallic copper resulting—$2 Cu_2 O, Cu_2 S = 3 Cu_2 + S O_2$. The copper so obtained is further purified by melting and directing upon it a current of air, and is finally *poled—i.e.*, melted under a layer of coal, and stirred by poles of green birch or oak. 3. By reducing oxide of copper in a current of hydrogen at a low red heat. 4. By precipitating copper from its solution by means of the galvanic current (electrolytic copper). 5. By precipitating a solution of sulphate of copper with scrap iron.

OXIDES OF COPPER.

Copper yields three oxides, of which, however, cupric oxide only yields stable oxygen salts.

Copper Quadrantoxide, . .	$Cu_4 O$.
Cuprous Oxide, . . .	$Cu_2 O$.
Cupric Oxide, . . .	$Cu O$.

Copper Quadrantoxide, $Cu_4 O = 270$.

In the hydrated condition, in which only it is known, this oxide is a green, very unstable powder, and has great affinity for oxygen. Oxygen acids decompose it into copper and cupric salts. It is insoluble in ammonia. It may be obtained by adding a solution of sulphate of copper to an excess of a solution of stannous chloride in caustic potash.

Cuprous Oxide, $Cu_2 O = 143$.

Occurrence.—Found native as *red copper ore* in regular octahedra, having a specific gravity of 3·85 to 6·15.

Properties.—Artificially prepared, it is a red powder; the more brilliant in colour the finer the powder. It is soluble in hydrochloric acid, yielding cuprous chloride, but is decomposed by oxygen acids into copper and cupric salts. It is soluble in ammonia, yielding a colourless solution if all oxygen has been excluded, but rapidly becoming blue on exposure to air. It is dissolved by melted glass, and imparts to it a beautiful red colour. It has great affinity for oxygen.

The hydrated oxide forms a yellow or orange-coloured powder.

Preparation—Anhydrous.—By heating sulphate of copper with finely divided copper; by reducing a solution of sulphate of copper with grape sugar in the presence of an alkali at a gentle heat. *Hydrated*—By precipitating a solution of cuprous chloride with caustic potash or soda; it loses its water at 360°.

Cupric Oxide, $Cu\,O = 79{\cdot}5$. Found native as *tenorite* or *melaconite*.

Properties.—A black amorphous powder or scales of specific gravity, 6·2 to 5·4, or regular tetrahedra of metallic lustre. All forms are readily soluble in acids yielding cupric salts. It readily parts with its oxygen when heated with combustible substances. The hydrated oxide constitutes either a blue [$Cu\,H_2\,O_2 = Cu\,O, H_2\,O$] or brown [$3\,Cu\,O, H_2\,O$] precipitate.

Preparation—Anhydrous.—1. By heating nitrate of copper; 2, by heating metallic copper to redness in a current of air. *Hydrated*—(*a*) $Cu\,H_2\,O_2$, by precipitating a solution of a cupric salt with a caustic alkali at ordinary temperature, and drying at the same temperature over oil of vitriol; (*b*) $3\,Cu\,O, H_2\,O$, by heating the first hydrate in contact with water to 100°.

CUPROUS SALTS.

Cuprous Chloride, $Cu_2\,Cl_2 = 198$.

Properties.—A white crystalline powder consisting of regular tetrahedra; it possesses great affinity for oxygen. It is insoluble in water; soluble in strong hydrochloric acid, and in ammonia; the latter solution absorbs various gases as carbonic oxide, acetylene, &c.

Preparation.—By boiling cupric chloride with strong hydrochloric acid and metallic copper, and precipitating by water, from which all air has been expelled by boiling.

Cuprous Sulphide, $Cu_2\,S = 159$.

Found native as *copper glance*, and combined with sulphide of iron in *copper pyrites* ($Cu_2\,S, Fe_2\,S_3$). Prepared by heating together 4 parts of copper and 1 part of sulphur, or by burning copper in sulphur vapour.

CUPRIC SALTS.

Cupric Carbonates.—All known cupric carbonates are basic salts. Some are found native, such as *malachite* [$Cu\,O, H_2\,O, Cu\,C\,O_3$], *mysorin* ($Cu\,O, Cu\,C\,O_3$), *azurite* [$2\,Cu\,C\,O_3, Cu\,O, H_2\,O$]. Others may be prepared artificially in the form of blue precipitates, becoming green on drying, by precipitating a cupric salt by means of an alkaline carbonate at various temperatures; others still are formed as a green coating on copper when this metal is exposed to the action of moist air containing carbonic anhydride, and constitute *verdigris*.

Cupric Sulphate (*blue vitriol*), $Cu\,S\,O_4, 5\,H_2\,O = 153{\cdot}5 + 90 = 243{\cdot}5$.

Properties.—This salt cyrstallises in blue crystals of the triclinic (doubly oblique) system. It loses four molecules of water at 100°, or *in vacuo* at 38°, becoming white; the fifth molecule can only be expelled at a temperature of 220° to 240°. It is very soluble in water, 100 parts of which dissolve at 10° 36·95 parts, at 52° 65·83 parts, and at 100° 203·32 parts. The dehydrated salt has great affinity for water, and may be used as a desiccating agent. It forms double salts with the alkaline sulphates.

Preparation.—By dissolving metallic copper in hot sulphuric acid. By roasting copper pyrites and extracting the roasted mass with water.

Cupric Sulphide, $Cu\,S = 95{\cdot}5$.

Occurrence.—Found native in hexagonal crystals of blue colour in indigo copper. Obtained as a blue powder by heating finely divided copper with flowers of sulphur to a temperature not exceeding the boiling point of sulphur, or as a black precipitate by passing sulphuretted hydrogen into a solution of impure salt.

Cupric Nitrate, $Cu\,(N\,O_3)_2 = 3\,H_2\,O\ 187{\cdot}5 + 54 = 241{\cdot}5$.

Properties.—Blue crystals which are very deliquescent, very soluble in water, and cannot be dried without decomposition. It is readily decomposed with liberation of nitric acid, and hence acts as a powerful oxidising agent. It leaves amorphous cupric oxide on heating.

Preparation.—By dissolving the metal or its oxide in nitric acid, and evaporating to crystallisation.

Cupric Chloride, $Cu\,Cl_2, 2\,H_2\,O = 134{\cdot}5 + 36 = 170{\cdot}5$.

Properties.—Square prismatic crystals of green colour, readily soluble in water, yielding a green solution; soluble also in alcohol and ether. When heated the crystals at first turn brown and become anhydrous, but on stronger heating break up into cuprous chloride and chlorine. It yields several oxychlorides with oxide of copper.

Preparation.—By dissolving cupric oxide in hydrochloric acid; by dissolving copper in strong hydrochloric acid with access of air; by dissolving copper in *aqua regia*.

Cupric Arsenite, $Cu\,H\,As\,O_3 = 187{\cdot}5$.

This salt is known as *Scheele's green.* It is a green powder obtained by precipitating a solution of sulphate of copper with arsenite of potassium; it is insoluble in water.

Cupric Hydride, $Cu_2\,H_2 = 129$.

This compound may be produced by precipitating sulphate of copper with hypophosphorous acid, at a temperature not exceeding 70°, and filtering rapidly. It is very unstable.

Ammonium Compounds of Copper.—Copper and its salts yield a variety of compounds containing ammonia, and these may be viewed as salts of ammonium, in which one or more atoms of hydrogen are replaced by copper, with or without an excess of ammonia. As, for example, *ammonio-sulphate of copper*, $4\,NH_3,\ CuSO_4,\ 2\,H_2O$, or $[(NH_4)_2\,SO_4,\ (NH_3)_2\,Cu\,H_2\,O_2]$. Obtained by adding ammonia in slight excess to a solution of sulphate of copper, and precipitating by addition of alcohol.

Cupros-ammonic chloride $(NH_3)_2{}'\ Cu'_2\ Cl_2$, and cuprammonic chloride $(NH_3)_2\,Cu''\,Cl_2$ are obtained by the action of ammonia on cuprous and cupric chloride, respectively.

General Character of Copper Compounds.—*Cuprous compounds* are generally colourless and insoluble in water, but soluble in hydrochloric acid and in ammonia, the solutions rapidly absorb oxygen and yield cupric compounds.

Cupric Compounds.—The hydrated compounds are either blue or green, the anhydrous compounds white or brown. Solutions of the salts give with *caustic alkalies* or ammonia a blue precipitate, soluble in excess of the latter, yielding a blue solution. *Sulphuretted hydrogen* gives a black precipitate, *ferrocyanide of potassium* a chocolate-coloured precipitate in neutral or slightly acid solutions. A clean piece of iron or steel immersed in an acidulated solution containing even a minute trace of copper only becomes coated after a time with a red coating of metallic copper. From any acidified solution of copper the metal is readily obtained in the metallic condition on the negative pole of a battery.

Physiological Action.—All cupric compounds are poisonous. The sulphate is used medicinally in small doses as an astringent and tonic, or in larger doses as an emetic.

THE NOBLE METALS.

MERCURY.	PALLADIUM.
SILVER.	IRIDIUM.
GOLD.	RHODIUM.
PLATINUM.	OSMIUM.
	RUTHENIUM.

MERCURY.*

(*Latin, hydragyrum; argentum vivum, quicksilver*), $Hg = 200$. *Specific gravity of liquid*, 13·6 (*water* = 1); *of vapour*, 100 ($H = 1$). *Specific heat*, 0·0333.† *Melting point*, $-39·5°$. *Boiling point*, 357·25°. *Dyad.*

Occurrence in Nature.—The chief occurrence of this metal is as *sulphide* in the mineral *cinnabar* (HgS), but it is also found *native* mixed with cinnabar, or more rarely amalgamated with gold or silver. It does not occur widely diffused, but in considerable deposits in various parts of the world, notably in the mines of Almaden in Spain, and of Idria in Austria, also in Bavaria, in California, in China, and in Japan. Mercury is also found rarely as chloride (calomel), iodide, selenide, &c.

Properties.—Mercury is the only metal which is liquid at ordinary temperatures. It is almost silver-white, of brilliant metallic lustre, and when pure is extremely mobile; separate drops readily coalesce when brought into contact with one another. Globules of the pure metal are spherical, and run over paper or porcelain surfaces without alteration of form, and without leaving a mark. It freezes at a temperature of $-39·5°$, and crystallises in regular octahedra. It boils under atmospheric pressure at a temperature of 357·25°, but volatilises at all temperatures. Its vapour is poisonous. It is permanent in air at ordinary temperatures, but oxidises to mercuric oxide (HgO) when kept for some length of time near its boiling point in contact with air. It also oxidises in the presence of ozone. It is insoluble in hydrochloric acid, or in cold sulphuric acid, but dissolves in the latter, when heated, with evolution of sulphurous anhydride. It is readily soluble in nitric acid; cold diluted acid in excess produces mercurous nitrate, but if the mercury is in excess a basic mercurous nitrate is produced; concentrated acid in excess dissolves it with evolution of nitric oxide, and production of mercuric nitrate.

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* So called by the alchemists, after the planet Mercury.

† Of solid between $-78°$ and $-40°$ 0·0319 (*Regnault*).

When mercury is triturated with grease, chalk, or various other substances, it may be obtained in an extremely fine state of division, in which it loses its metallic appearance and assumes a dull black or grey colour (deadening of mercury). In this state it oxidises even at ordinary temperature, and *grey powder*, *chalk and mercury*, when kept for some time, frequently contains a considerable proportion of mercuric oxide; in this way the comparatively mild *grey powder* becomes converted into a dangerously poisonous compound.

Uses.—Mercury is used for the manufacture of thermometers, barometers, and other physical apparatus; for the collection of gases soluble in water; the preparation of mirrors (see tin, p. 299); for the extraction of gold and silver from their ores, and for the preparation of mercurous compounds used in the arts and in medicine.

Manufacture and Preparation.—The cinnabar is either roasted in a current of air, whereby it is converted into mercury and sulphurous anhydride, or is mixed with lime or iron and heated, mercury and sulphides of lime or iron resulting. The mercury is condensed in stone chambers or stoneware bottles called *aludels*. It generally comes into commerce in wrought-iron bottles.

To prepare pure mercury, commercial mercury is carefully distilled; or is agitated repeatedly with dilute nitric acid, or for some time covered with a layer of concentrated sulphuric acid.

Amalgams.—Many metals combine with mercury yielding alloys which are known as *amalgams.** These amalgams are liquid at ordinary temperatures in presence of an excess of mercury, but are otherwise solid or semi-solid. In some cases the metal readily unites with the mercury at ordinary or slightly elevated temperatures, such as gold, silver, tin, the alkali metals, &c.; in other cases the union may be brought about by immersing the metal in a solution of a salt of mercury, as in the case of copper, or by making mercury the negative pole of a battery while immersed in a solution of a salt of the metal, the amalgam of which is to be produced, or by acting on such a solution with an amalgam of sodium.

OXIDES OF MERCURY.

Mercury forms two compounds with oxygen—

Mercurous oxide, Hg_2O.
Mercuric oxide, HgO.

Both oxides yield salts, and are distinguished by the readiness with which they form basic salts.

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* Supposed to be an alchemist's anagram of *μαλαγμα*, an emollient.

Mercurous Oxide (*suboxide of mercury*), $Hg_2\,O = 416$.

Properties.—A dark grey or black heavy powder, insoluble in water, soluble in acid yielding mercurous salts. Decomposed slowly by the action of light, or rapidly at a temperature of 100° into mercuric oxide and mercury.

Preparation.—By precipitating a mercurous salt with caustic potash or soda and filtering, washing, and drying in the dark at ordinary temperatures.

Mercuric Oxide (*mercury monoxide, red oxide of mercury*), $Hg\,O = 216$.

Properties.—Dark or light red, crystalline, or yellow, amorphous powder, according to its preparation. Very slightly soluble in water imparting to it an alkaline reaction. The crystalline varieties are far less readily acted on by chemical agents than the amorphous variety, particularly when freshly precipitated or dried only at a low temperature. When strongly heated it is decomposed into metallic mercury and oxygen; heated with substances capable of taking up oxygen it acts as a powerful oxidising agent.

Preparation.—*Crystalline*—By heating mercury to near its boiling point in contact with air; by heating a mixture of mercuric nitrate and mercury as long as red fumes are evolved. *Amorphous*—By precipitating a solution of a mercuric salt with caustic potash or soda or lime water.

MERCUROUS SALTS.

Mercurous Nitrates.—The normal nitrate, $Hg_2\,(N\,O_3)_2,\ 2\,H_2\,O = 560$, is obtained by gently warming an excess of metallic mercury with nitric acid, diluted with 2 or 3 times its volume of water, and allowing to crystallise. It forms colourless crystals belonging to the monoclinic system, which lose all their water *in vacuo* over oil of vitriol. It dissolves in a small quantity of water, but much water decomposes it into nitric acid, and a basic salt (di-mercuro hydric-nitrate), $Hg_2\,H\,N\,O_4$, which forms a yellow crystalline precipitate. By heating crystals of the normal nitrate with their mother liquor and mercury, colourless rhombic prisms of another salt (mercurous hydro-trinitrate) are formed, $Hg_4\,(N\,O_3)_3\,H\,O$. Other nitrates are known. The normal nitrate yields many double salts with the nitrates of other metals.

Mercurous Sulphate, $Hg_2\,S\,O_4 = 496$.

Properties.—A white crystalline mass, slightly soluble in water, which can be sublimed by careful heating.

Preparation.—By gently heating sulphuric acid with excess of metallic mercury; or by precipitating a solution of mercurous nitrate with diluted sulphuric acid.

Mercurous Chloride (*calomel*), $Hg_2\,Cl_2 = 471$. *Specific gravity*, 7·1 (*water* = 1); *of vapour*, 117·75 ($H = 1$).

Occurrence in Nature.—Found native as the mineral *horn-quicksilver*, crystallised in the right prismatic system, and having a specific gravity of 6·4 to 6·5.

Properties.—A white amorphous powder or fibrous crystalline mass, according to mode of preparation. Insoluble in water,* alcohol, and cold dilute acids; readily soluble in boiling nitro-hydrochloric acid, with formation of mercuric chloride; boiling hydrochloric acid converts it into mercuric chloride and metallic mercury. Caustic potash decomposes it with formation of black mercurous oxide and potassium chloride. When heated it sublimes without fusion but dissociates, the vapour consisting of mercuric chloride and mercury, which on cooling re-combine.

Preparation.—By precipitating a solution of mercurous nitrate by means of hydrochloric acid; by heating together 4 parts of mercuric chloride, and 3 parts of mercury; when the vapour of these two substances is conducted into a large brick chamber, the calomel condenses as a fine white powder, but when the vapour is condensed on a cold surface the calomel is obtained as a fibrous crystalline mass. When produced by sublimation it must be carefully washed with warm water in order to remove the last traces of mercuric chloride.

Mercurous Iodide (*green iodide of mercury*), $Hg_2\,I_2 = 654$.

A yellowish-green powder, which melts at 290°, but may be sublimed below this temperature, yielding yellow rhombic crystals. When heated it turns red, but re-assumes its original colour on cooling. It is sparingly soluble in water, insoluble in solution of iodide of potassium, but is gradually changed in contact with it into mercuric iodide and mercury.

Preparation.—1. By triturating 10 parts of mercury, with 6·7 parts of iodine with the addition of alcohol. 2. By precipitating a solution of a mercurous salt with iodide of potassium.

MERCURIC SALTS.

Mercuric Carbonates.—Several basic mercuric carbonates are known, such as $4\,HgO,\ CO_2$ and $3\,HgO,\ CO_2$, and may be produced by adding a solution of mercuric chloride to a large excess of an alkaline carbonate or sesqui-carbonate. They form brown amorphous powders.

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* Long continued boiling with water decomposes it into mercuric chloride which dissolves, and metallic mercury which is precipitated.

Mercuric Nitrates.—Several nitrates are known. The normal salt, $Hg(NO_3)_2, 8H_2O$, may be obtained in colourless rhombic crystals, by cooling a solution of mercuric nitrate in nitric acid to – 15°; the salt melts in its water of crystallisation at ordinary temperatures, and changes into a basic salt, $Hg(NO_3)_2 HgO, 2H_2O$. Both these salts are decomposed by treatment with water, yielding more and more basic nitrates according to the amount of water used and its temperature, and finally mercuric oxide only is left.

Mercuric Sulphate, $HgSO_4, H_2O = 296 + 18 = 314$.

This salt may be obtained in colourless crystals by treating metallic mercury with hot sulphuric acid, heating to expel excess of acid, adding a small quantity of water to the crystalline mass left, and allowing to stand for some time. By treatment with much water the salt is decomposed into free sulphuric acid and a difficultly soluble heavy yellow powder consisting of basic sulphate, formerly employed medicinally and known as *turpeth mineral*, $HgSO_4, 2HgO$.

Mercuric Sulphide (*cinnabar*), $HgS = 232$. *Specific gravity,* 6·287 (*water* = 1).

Occurrence in Nature.—Found native in crystals belonging to the hexagonal system, or in granular or earthy masses constituting the chief ore of mercury.

Properties.—A red crystalline mass or black amorphous powder according to mode of preparation. Insoluble in hydrochloric, nitric, or sulphuric acids, soluble in nitro-hydrochloric acid. Insoluble in sulphide of ammonium, but soluble in alkaline sulphides in presence of free alkali. Can be sublimed without decomposition out of contact with air. Yields a white compound with mercuric chloride.

Preparation.—By triturating mercury and sulphur, or by precipatating a mercuric salt, black amorphous sulphide is obtained, which, when sublimed out of contact with air, or when digested with a warm solution of an alkaline persulphide, changes to red. When sulphuretted hydrogen is passed into a solution of mercuric chloride, a white precipitate is thrown down at first consisting of $HgCl_2 2HgS$, which by the further action of sulphuretted hydrogen becomes orange, and is finally changed into the black sulphide.

Mercuric Chloride (*corrosive sublimate*), $HgCl_2 = 271$. *Specific gravity,* 5·4 (*water* = 1); *of vapour,* 135·27 ($H = 1$). *Melting point,* 288°; *boiling point,* 303°.

Properties.—This salt crystallises in needles belonging to the rhombic system. It requires about fourteen times its weight of cold, but only twice its weight of boiling water for solution; 100 parts of water dissolve 6·57 parts of the salt at 10°, and 53·96 parts at 100°. It is also soluble in alcohol and in ether.

On heating it sublimes unchanged. It forms double salts with the chlorides of the alkali metals, which are more soluble than mercuric chloride itself. It is a powerful antiseptic.

Preparation and Formation.—1. By heating a mixture of mercuric sulphate and sodium chloride. 2. By dissolving mercuric oxide in hydrochloric acid. 3. By acting on mercury with *aqua regia.* 4. By burning the metal in chlorine.

Physiological Action.—Irritant and corrosive, and highly poisonous; in very small doses, alterative.

Mercuric Iodide (*red iodide of mercury*), $HgI_2 = 327$.

Occurrence in Nature.—Found native as the mineral *coccinite.*

Properties.—Two modifications of this iodide are known, one red, the other yellow, but the former only is stable at ordinary temperatures. The red variety crystallises in square prismatic octahedra, which when heated to 150° become yellow, and melt at 238° to a yellow liquid, which on further heating volatilises, the vapour condensing to beautiful yellow crystals belonging to the right prismatic system. At ordinary temperatures these yellow crystals change more or less rapidly into the red variety with evolution of heat. The slightest injury to a yellow crystal, such as touching it with the point of a pin, instantly changes it to red. Both modifications are readily soluble in alcoholic solutions of iodide of potassium, or chloride of mercury, yielding colourless solutions; but are insoluble in water. Mercuric iodide yields, with the iodides of potassium and ammonium, yellow crystalline compounds, $2\,HgI_2, KI, 2\,H_2O$ and $2\,HgI_2, NH_4I, 2\,H_2O$.

Preparation.—By triturating 10 parts of metallic mercury with 13 parts of iodine with the addition of a little alcohol; by precipitating mercuric chloride with iodide of potassium. In the latter case the precipitate is at first yellow but speedily turns red. By exposing metallic mercury to the action of iodine vapour, the product is yellow at first but speedily turns to red.

Mercuric Cyanide, $Hg\,Cy_2$.—This salt may be obtained in colourless crystals of the square prismatic system. When heated it breaks up into mercury and cyanogen. It is prepared by dissolving mercuric oxide in hydrocyanic acid and evaporating to crystallisation.

Ammonium Compounds of Mercury — *Mercurammonium Salts.* — By the action of ammonia or of ammonium salts on salts of mercury, compounds are produced which may be regarded as ammonium salts, in which one or more atoms of hydrogen are replaced by mercury, either in its pseudo-monad or dyad condition. A few only can be mentioned:—*Mercuros-diammonic chloride* $(N H_3 Hg')_2 Cl_2$, a black powder obtained by the action of ammonia gas on mercurous chloride. When heated it breaks up into ammonia and mercurous chloride. *Mercuros-ammonic chloride*, $N H_2 Hg'_2 Cl$, a grey powder formed by digesting calomel in aqueous ammonia. *Mercuri-ammonic chloride*, $N H_2 Hg'' Cl$ (*infusible white precipitate*), produced by precipitating a solution of mercuric chloride with excess of ammonia; when heated it is decomposed without fusion. *Mercuri-diammonic dichloride* $(N H_3)_2 Hg'' Cl_2$ (*fusible white precipitate*), obtained crystallised in colourless dodecahedra by adding a solution of mercuric chloride to a boiling solution of ammonium chloride and ammonia, until a permanent precipitate begins to be formed, and allowing to cool. When heated the crystals first melt and then decompose.

General Character of Mercury Compounds.—Mercury compounds containing a colourless acid are generally white when normal, yellow when basic. A solution of any mercury compound deposits metallic mercury on a piece of metallic copper immersed in it, particularly on boiling, or on gold when this metal is touched, through the solution, with a piece of iron or steel. The deposit when heated is volatilised, and condenses on cold surfaces, such as the inside of a glass-tube, in minute globules, recognisable as such under the microscope, and which are changed into yellow iodide, speedily changing into the red modification when a small fragment of iodine is volatilised in the tube. All mercury compounds when heated in a test-tube with dry carbonate of soda yield a sublimate of metallic mercury.

Mercurous Compounds, whether soluble or insoluble in water, when acted on by *caustic potash* yield black mercurous oxide. Soluble salts yield with *hydrochloric acid* a white precipitate, which is turned black by ammonia; iodide of potassium yields a green precipitate of mercurous iodide.

Mercuric compounds yield with *caustic alkalies* a yellow precipitate of mercuric oxide; *ammonia* produces a white precipitate of a mercurammonium compound. *Sulphuretted hydrogen* yields a precipitate, which is white or orange in the presence of an excess of the salt, black with an excess of sulphuretted hydrogen. The precipitate is insoluble in sulphide of ammonium or in nitric or hydrochloric acid, but soluble in *aqua regia*. *Iodide of potassium* yields a red precipitate readily soluble in excess of the precipitant, and also slightly soluble in mercuric chloride solution. *Stannous chloride* produces a white precipitate of mercurous chloride, which in presence of excess of the precipitant becomes grey or black, being converted into metallic mercury.

Physiological Action.—All compounds of mercury, but more particularly the mercuric compounds, are poisonous; some, like corrosive sublimate, are violent corrosive poisons. Some are employed as caustics, disinfectants, and antiseptics; others as purgatives or alteratives

SILVER.*

(*Latin*, *argentum*), *Ag* = 108. *Specific gravity* = 10·57 (*water* = 1). *Specific heat* = 0·0560. *Melts at about* 1000°. *Monad.*

Occurrence in Nature.—Silver is found both native and in combination. In the form of sulphide as *silver glance*, Ag_2S; as chloride in *horn silver*, $AgCl$; as sulphantimonite in *pyrargyrite*, $3Ag_2S, Sb_2S_3$; as sulpharsenite in *proustite*, $3Ag_2S, As_2S_3$; and in combination with bromine, iodine, tellurium, &c. Galena, the principal ore of lead, almost always contains traces of silver, and frequently forms a considerable source of the metal. Silver is also found in minute traces in sea water.

Properties.—Silver is the whitest of all metals, and admits of the highest degree of polish. It is very ductile and extremely malleable, so that it can be beaten out into leaves so thin that they become translucent and transmit a bluish light. It is the best conductor of heat and electricity. It melts at a temperature of about 1000°, and can be distilled at a white heat. Melted in contact with air it absorbs about 22 times its volume of oxygen, which is given off again as the metal solidifies; the solid film first formed on the surface of the melted mass is thrown up or burst by the escaping gas, frequently causing loss of silver (spitting of silver). It crystallises in regular octahedra. Silver is permanent in pure air at all temperatures, but tarnishes very readily in air containing a minute trace of sulphuretted hydrogen. It is insoluble in hydrochloric acid, but dissolves in hot concentrated sulphuric acid with evolution of sulphurous anhydride, and readily in nitric acid, with evolution of nitric oxide. It is not acted on even by melted caustic alkalies.

Silver is rarely used in the pure state, as it is too soft, and is therefore generally alloyed with other metals, chiefly copper. English standard silver is an alloy of 92·5 parts silver and 7·5 parts copper, or, as it is technically expressed, has a fineness of 925—that is, there are 925 parts of silver in 1000 parts of the alloy.

Silver is also largely used for coating other metals (silver-plating), which is now nearly always done by electro-deposition (electro-plating).

* Anglo-Saxon, *seolfor*, *silfer*.

It is further used for silvering glass for the production of mirrors. In the case of mirrors for ordinary use, the film of silver is at the back of the glass, as in the old mercurial mirrors, while in the concave reflectors for astronomical telescopes the film is on the front surface and reflects the light directly.

Extraction—1. *From Galena.*—All the silver contained in this lead ore will be found in the lead produced from it, and, if present in sufficient quantity, $\frac{1}{10}$ per cent. and upwards, the lead is at once submitted to cupellation, that is, the lead is converted into oxide by submitting it—melted in a reverberatory furnace, the concave hearth of which is lined with burnt clay or bone ash—to a rapid current of air. The lead is in this way removed in the form of oxide, the silver only remaining. If the silver amounts to less than $\frac{1}{10}$ per cent., it has first to be concentrated, which may be done by *Pattinson's process.* This consists in allowing the melted lead to cool slowly, so that it crystallises and removing the lead crystals as they are formed; the greater part of the silver remains in the fluid lead; if necessary, this process is several times repeated, until the silver has been sufficiently concentrated, when the lead is submitted to cupellation. Silver thus admits of profitable extraction, even when not present in greater proportion than 2 or 3 ounces to the ton.

2. *From other silver ores.*—The ore, generally a sulphide of silver, is either roasted with common salt and then worked in revolving casks with iron and mercury, or ground fine, mixed with water and salt, and, after standing for some days, some crude iron and copper sulphates (magistral), obtained by roasting copper pyrites, are added and the whole mixed, after which the silver is extracted by means of mercury; the whole of the mixing, &c., is effected by the treading of mules. From the amalgam thus produced by either process, silver is obtained by driving off the mercury by distillation.

OXIDES OF SILVER.

Silver yields three oxides, of which, however, argentic oxide only yields stable salts.

Argentous oxide (*quadrantoxide*), . .	Ag_4O.
Argentic oxide, ...	Ag_2O.
Argentic peroxide, ...	Ag_2O_2.

All three oxides, when heated, yield metallic silver.

Argentous Oxide, $Ag_4O = 448$.

A black powder, soluble in hydrogen acids, with formation of the corresponding halogen compound, but decomposed by oxygen acids into metallic silver and the particular argentic salt.

Argentic Oxide (*silver monoxide*), $Ag_2 O = 232$. *Specific gravity* = 7·35.

Properties.—A brown or black powder, soluble in about 3000 parts of water, to which it imparts a distinctly alkaline reaction. Heated to 250°, it breaks up into silver and oxygen. In the dry state it is a powerful oxidising agent, yielding inflammable or explosive mixtures, with various oxidisable substances, such as sulphur, amorphous phosphorus, sulphide of antimony, &c. It is a powerful base, and distinguished by the fact that it readily yields anhydrous normal salts with acids. Freshly-precipitated argentic oxide is very readily soluble in ammonia, and this solution, when evaporated at a gentle heat, yields crystals of *fulminating silver*, probably of the composition, $N H_2 Ag$, which are most violently explosive at the slightest touch.

Preparation.—By precipitating a solution of nitrate of silver with caustic alkalies, or by boiling freshly-precipitated chloride of silver with a strong solution of caustic potash. The freshly-precipitated moist oxide is probably a hydrate, $Ag H O$, and is more active than when dried.

Argentic Peroxide (*silver dioxide*), $Ag_2 O_2 = 248$.

A black powder, produced by the action of ozone on silver; it is a more powerful oxidising agent than the monoxide.

SALTS OF SILVER.

Argentic Carbonate, $Ag_2 C O_3 = 276$.

This salt is precipitated white by the addition of an alkaline carbonate to a solution of argentic nitrate.

Argentic Nitrate (*lunar caustic*), $Ag N O_3 = 170$.

Properties.—This salt crystallises in colourless tabular crystals of the rhombic system. It melts at a temperature of 193°, and solidifies to a crystalline mass on cooling (lunar caustic). It is soluble in half its weight of water, at ordinary temperatures forming a neutral solution; and in 4 parts of alcohol. When pure, it is not altered by exposure to light, but is readily decomposed, and turns black in contact with organic matter; hence it stains the skin to which it is applied black, and forms the basis of most indelible marking inks.

Physiological Action.—Nitrate of silver acts as a powerful caustic on animal matter, and is frequently used as such in surgery.

Preparation.—By dissolving pure silver in dilute nitric acid, and evaporating to crystallisation. By dissolving standard silver in nitric acid, evaporating, and heating sufficiently to decompose the nitrate of copper, extracting the heated mass with water and crystallising.

Argentic Nitrite, $Ag\,N\,O_2 = 154$.

A difficultly soluble salt, which is precipitated when a solution of nitrate of silver is added to a solution of nitrite of potassium. It forms an excellent basis for obtaining solutions containing a definite proportion of nitrite (p. 124).

Argentic Sulphate, $Ag_2\,S\,O_4 = 312$.

A difficultly soluble salt, which may be obtained by dissolving silver in hot concentrated sulphuric acid, or by precipitating a strong solution of nitrate of silver by sulphuric acid. Soluble in 200 parts of cold water.

Argentic Sulphide, $Ag_2\,S = 248$.

Found native as silver glance, crystallised in the regular system. Specific gravity, 7·196. Produced as a black precipitate by the addition of sulphuretted hydrogen to a solution of a silver salt, or as a dark coating on silver, by the action of gaseous sulphuretted hydrogen on metallic silver. Found in small proportions or traces in nearly all galena.

Argentic Choride, $Ag\,Cl = 143{\cdot}5$.

Found native as the mineral *horn silver*, crystallised in the regular system. Specific gravity, 5·55 to 5·6.

Properties.—A white curdy precipitate or white powder speedily becomes violet on exposure to light. It melts at a temperature of 260° to a clear yellow liquid, which solidifies to a translucent horny mass. It is insoluble in water and dilute acids, slightly soluble in concentrated hydrochloric acids and solutions of alkaline chlorides; readily soluble in ammonia and in a solution of thiosulphate of sodium ($Na_2\,S_2\,O_3$). When moist, it is readily reduced to the metallic state by contact with zinc or iron; also readily reduced by fusion with alkaline carbonates.

Preparation.—By precipitating a solution of nitrate of silver or any soluble silver salt, by hydrochloric acid or any soluble chloride. By roasting sulphide of silver with chloride of sodium.

Argentic Bromide, $Ag\,Br = 188$.

Bromide of silver closely resembles the chloride, and may be obtained as a yellow precipitate in an analogous manner. Found native as the mineral bromide. Specific gravity, 5·8 to 6.

Argentic Iodide, $Ag\,I = 235$.

Found native as the mineral iodide. Specific gravity, 5·5.

A pale yellow curdy precipitate, insoluble in dilute acids and in ammonia, but turned white by the latter; soluble also in thiosulphate. Melts at a dull red heat, and solidifies to a yellow mass, having a specific gravity of 5·687; the precipitate has a specific gravity of 5·8. Pure iodide of silver is not blackened by light, but acquires the property of precipitating metallic silver on its surface in presence of a reducing agent. The dry iodide absorbs ammonia, yielding the compound $2AgI, NH_3$. When gently heated, the ammonia is expelled, and the compound forms a very convenient means of producing liquid ammonia on a small scale by heating it enclosed in a Faraday tube (p. 127).

Preparation.—By precipitating a soluble silver salt with a soluble iodide.

Both dry bromide and iodide of silver are converted into the chloride by gaseous chlorine, or by gaseous hydrochloric acid, at temperatures above 700°. On the other hand, aqueous solutions of an iodide or of hydroiodic acid convert both bromide and chloride of silver into iodide (see table of thermal values, p. 348).

Argentic Cyanide, $Ag\,Cy = 134$.

A white curdy precipitate, closely resembling the chloride and bromide of silver, but decomposed when heated into metallic silver, paracyanogen and cyanogen. Cyanide of silver is readily soluble in a solution of cyanide of potassium, and such a solution is best adapted for use in electro-plating, and is largely employed for this purpose. The solution contains a double cyanide of potassium and silver, $Ag\,Cy, K\,Cy$, which can be obtained in the crystalline form.

Preparation.—By the careful addition of a solution of cyanide of potassium to one of nitrate of silver; addition of excess of the cyanide redissolves the precipitate first formed.

General Characters of Silver Salts.—Silver salts are colourless with colourless acids. When fused with carbonate of soda they yield metallic silver. Solutions of silver salt give with *hydrochloric acid* or *soluble chlorides* a white curdy precipitate, insoluble in acid, readily soluble in ammonia. *Caustic alkalies* or *ammonia* throw down a dark-brown precipitate of oxide very readily soluble in ammonia. *Sulphuretted hydrogen* gives a black precipitate of sulphide insoluble in sulphide of ammonium.

Physiological Action.—Silver salts act as violent irritant poisons, and the nitrate is a powerful caustic, or in dilute aqueous solution an astringent.

GOLD.*

(*Latin*, *aurum*), *Au* = 197. *Specific gravity*, 19·26 *to* 19·55. *Specific heat*, 0·0324. *Melting point*, 1250°. *Monad and Triad.*

Occurrence in Nature.—Gold is found somewhat widely diffused, but in small quantity only. It occurs chiefly native, often crystalline (regular system) or in irregular masses termed nuggets, or disseminated in quartz veins, or as grains and dust in alluvial deposits, in river-sands, &c. It is frequently found alloyed with silver; it is also found combined with bismuth, tellurium, mercury, &c., in a few rare minerals. It occurs in traces in many ores of silver, copper, lead, pyrites, &c.

Properties.—Gold is one of the few metals showing a decided colour, namely, a brilliant yellow (gold yellow), and admits of high polish. It is the most malleable and ductile of all the metals, and can be drawn into wire so fine that 500 feet weigh only a single grain, and can be beaten out into leaf only $\frac{1}{300,000}$ of an inch in thickness. Such leaves transmit a blue or green light. It is permanent in dry or moist air at all temperatures, and is not acted on by any single acid except selenic; it is, however, readily soluble in nitro-hydrochloric acid, and in chlorine or bromine water. It readily combines with chlorine or bromine at ordinary temperatures. Most metals and nearly all reducing agents precipitate it in the metallic state from its solutions.

Gold is used chiefly in the form of metal, for coinage, for ornaments, and for gilding, either as gold leaf in the case of non-metallic surfaces, or electrolytically in the case of metals. Pure gold, however, is employed only in the manufacture of gold leaf, or in the preparation of the solutions employed in electro-plating, for which purpose a solution of the double cyanide of gold and potassium ($Au\,Cy_3$, $K\,Cy$) is used. For coins or ornaments, pure gold would be too soft, and is therefore alloyed with copper or silver or both. The composition of such an alloy is expressed in *carats* or parts in 24, or in parts per mille (fineness). Thus English standard gold is composed of 11 parts of gold to 1 of copper (22 carat gold), or has a fineness of 916·66; other alloys are frequently used for making ornaments.

Extraction and Preparation.—From alluvial deposits or sand, in the first place, by washing away the light particles of sand and soil by means of water, the heavy gold particles remaining behind; from quartz rock by reducing it to a fine powder in stamping mills, and as above, washing away the light rock leaving the heavy gold behind.

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* Anglo-Saxon *gold* allied to *geolu*, yellow.

In both cases the gold from the heavier portions left behind by the water is extracted by means of mercury, and the mercury distilled off. The impure gold may be refined by melting it under borax, and passing through it a current of chlorine; by this means silver is removed and recovered in the form of chloride rising to the top of the melted gold, while other metallic impurities are volatilised in the form of chlorides. Perfectly pure gold is best obtained by dissolving refined gold in *aqua regia*, precipitating the gold by means of ferrous sulphate, and melting the finely divided gold so obtained under a mixture of borax and nitre.

OXIDES OF GOLD.

Gold forms two oxides, neither of which, however, yield simple salts with acids, although a few double salts of gold and some other metal are known. Both oxides are very readily decomposed into their elements at temperatures between 150° and 245°.

Aurous Oxide, $Au_2 O = 410$, is obtained as a violet-black powder by digesting aurous chloride ($Au Cl$) with a dilute solution of caustic potash. Hydrochloric acid converts it into auric chloride and metallic gold.

Auric Oxide, $Au_2 O_3 = 442$, is obtained as a brown powder by digesting a solution of auric chloride with magnesia, dissolving the precipitate of magnesium aurate ($Mg Au_2 O_4$) in nitric acid, and adding water to the solution; auric hydrate, $Au H_3 O_3$ ($Au_2 O_3 3 H_2 O$), is thrown down, which, by very gently heating, is converted into auric oxide. It is partially decomposed even at a temperature of 100°, and completely so at 245°. It dissolves in hydrochloric acid, yielding auric chloride. In caustic potash, it dissolves with formation of an aurate of potassium, $K Au O_2 3 H_2 O$, and when acted on by aqueous ammonia yields *fulminating gold*, the composition of which is not accurately known, but which, no doubt, is an ammonium compound, in which part of the hydrogen of the ammonium is replaced by gold.

SALTS OF GOLD.

Aurous Chloride, $Au Cl = 232{\cdot}5$.

Obtained by heating auric chloride to 185°; it is very readily decomposed into auric chloride and gold even by the action of water alone.

Auric Chloride (*terchloride of gold*), $Au Cl_3 = 303{\cdot}5$.

Obtained by the action of chlorine on gold, or by dissolving gold in *aqua regia.* On evaporating this solution, and carefully drying the residue at 150°, the anhydrous chloride is obtained; while if this hot saturated solution is allowed to cool, orange-coloured, needle-shaped crystals of the hydrated chloride ($AuCl_3$, $2H_2O$) are deposited. Heated to 185°, auric chloride is decomposed into aurous chloride and chlorine, but in an atmosphere of chlorine it may be sublimed unchanged at a temperature of 300°.

Auric chloride produces double chlorides with numerous other metallic chlorides, and also with the chlorides of many vegetable alkaloids.

Purple of Cassius.—By adding a solution of the mixed bi- and tetrachlorides of tin to a solution of auric chloride, a purple precipitate is obtained, which is called purple of Cassius. The composition of this precipitate is not known with certainty, and it probably varies under varying conditions of concentration, temperature, &c. The precipitate dissolves in melted glass, imparting to it a magnificent red tint; it is also used for painting on porcelain; it forms the most delicate test for the detection of gold in solution.

Characters of the Compounds of Gold.—Compounds of gold are generally yellow, orange, or red; they are all decomposed, leaving metallic gold when heated to redness, in presence of air. Solutions of gold yield a precipitate of metallic gold with most reducing agents; the precipitate in some cases (as for example, when produced by the action of phosphorus) is so fine that it remains suspended for a long time, yielding a mixture which appears clear and of a beautiful red or blue colour by transmitted light, but turbid by reflected light. A mixture of stannous and stannic chlorides produces a characteristic precipitate of purple of Cassius (see above).

PLATINUM.*

Platinum, Pt = 197·4. *Specific gravity,* 21·7 (*water* = 1). *Specific heat,* 0·0311. *Melts in the oxyhydrogen blowpipe at a temperature of about* 2000°. *Dyad and tetrad.*

Occurrence in Nature.—Platinum is found only native, that is, in the metallic condition, but always alloyed with other metals. Like gold, it is found in small grains, or, but rarely, in nuggets in alluvial deposits and in the sand of rivers. Its chief sources are the Ural mountains, but

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* French, *platine*, from old French, plate, silver; in allusion to its silvery appearance.

very small quantities are also found in California, Peru, Borneo, and minute traces occur in the auriferous sand of the Rhine.

Extraction and Preparation.—The alluvial deposits or river sands are first washed in running water to carry off the lighter particles, as in the case of gold, and a sand very rich in metal is thus obtained. This is first digested with dilute *aqua regia* to extract the gold; it is then boiled with strong *aqua regia* as long as anything is dissolved. The soluble portion contains all the platinum; an insoluble alloy consisting of osmium and iridium remaining behind. The solution is then mixed with a solution of chloride of ammonium, which throws down the platinum as the double chloride of platinum and ammonium ($Pt\,Cl_4\,2\,N\,H_4\,Cl$), together with traces of iridium. The double chloride is then heated, when it breaks up into chloride of ammonia and chlorine, which escape, and metallic platinum, which remains behind, in the form of a fine spongy mass. This spongy mass is first pressed into cakes under powerful pressure, and the cakes are heated to a white heat and moulded into an ingot under the hammer; or the metal may be melted by means of the oxyhydrogen or oxy-gas blowpipe in a lime crucible.

Pure platinum may be obtained from the commercial metal by dissolving it in *aqua regia*, boiling off excess of acid, and precipitating the platinum and iridium in the form of hydrated oxides by the addition of caustic soda. The liquid is boiled after the addition of some alcohol, and redissolved in hydrochloric acid. The solution so obtained contains the iridium in the form of a chloride not precipitated by chloride of ammonium; addition of this, therefore, throws down the platinum, but leaves the iridium in solution. The ammonium platinum chloride is collected, washed, dried and ignited, when pure platinum is left behind.

Properties.—Platinum is a greyish-white metal, admitting of a very high polish. It is permanent in dry or moist air at all temperatures. It is very malleable and highly ductile, and, like iron, it can be welded. Platinum is not acted on by any single acid, but dissolves in *aqua regia* or chlorine water; melted caustic alkalies, more particularly caustic lithia, readily attack it, and many metals form with it easily fusible alloys; silicon, phosphorus, and carbon also readily unite with it at a high temperature. Vessels made of platinum should, therefore, never be brought into contact with any of these substances at an elevated temperature. The metal is infusible at the temperature of any of our furnaces, but melts readily in the oxyhydrogen blowpipe. Molten platinum possesses the power, like silver, of absorbing oxygen, and like that metal, gives it off on solidifying. At a red heat the metal is readily permeated by hydrogen, owing to its property of dissolving that gas, but is not penetrated by oxygen or nitrogen and other gases. One of the most remarkable properties of metallic platinum is the power it possesses of condensing gases on its surface, but this power depends greatly on the physical condition of the metal. When in the form of foil or wire this property is noticeable chiefly at slightly elevated temperatures, many inflammable gases and vapours unite with oxygen at the surface of such platinum at temperatures far below their igniting point; when finely divided, as in the form of spongy platinum obtained by heating ammonium platinum chloride, or still more so, in the form of platinum black, as obtained by reducing the metal from its solution by various reducing agents, this power is very greatly increased, and many gases, vapours, and even liquids unite with oxygen with all the phenomena of ignition when brought into contact with this form of platinum in presence of air, even at ordinary temperatures.

Platinum is used chiefly in the metallic condition, either pure or alloyed with a small proportion of iridium, which renders it somewhat harder. It is thus used in the laboratory in the form of evaporating dishes, crucibles, foil, and wire. The retorts used for the final concentration of sulphuric acid are also frequently made of platinum. Its marked electro-negative character is made use of in Grove's battery.

OXIDES AND SALTS OF PLATINUM.

The compounds of platinum have, on the whole, been but little studied. The metal forms two oxides—platinous oxide, $Pt\,O$, and platinic oxide, $Pt\,O_2$, and their hydrates, $Pt\,H_2\,O_2$, and $Pt\,H_2\,O_4$; both oxides are basic, but the second also acts as an acid-forming oxide; they are both decomposed into metal and oxygen at higher temperatures. There are also two corresponding sulphides and chlorides, of which, platinum chloride, $Pt\,Cl_4$, is perhaps the best known of all the platinum compounds.

Platinic Chloride (*platinum tetra-chloride*), $Pt\,Cl_4 = 339{\cdot}4$.

Crystallised from water, platinic chloride is obtained in red non-deliquescent crystals of the composition, $Pt\,Cl_4, 5\,H_2\,O$, while, when crystallised from a solution containing much hydrochloric acid, it is obtained in brownish-red deliquescent crystals of the composition, $Pt\,Cl_4, 2\,H\,Cl, 6\,H_2\,O$. Both compounds are soluble in alcohol and ether in the cold, but are reduced when the solutions are warmed. When carefully heated, platinic chloride loses two atoms of chlorine, and becomes reduced to platinous chloride; when strongly heated it yields metallic platinum and chlorine.

Platinic chloride is remarkable for the ease with which it forms double chlorides with the chlorides of the alkalies and alkaline earth metals, with thallium, and with the chlorides of many vegetable alkaloids. These latter, as well as the double chlorides, with potassium, cerium, rubidium, and ammonium, are difficultly soluble, particularly in alcohol, and may be used for the separation of these compounds from solutions. These double chlorides have all the composition, $Pt\,Cl_4, 2\,M'\,Cl$, where M stands for a monad metal or compound radical.

Preparation.—By dissolving platinum in *aqua regia*, evaporating, gently heating the residue to expel excess of acid, adding water and crystallising from it, or crystallising directly from the acid solution when the compound, $Pt\,Cl_4,\ 4\,H\,Cl,\ 6\,H_2\,O$, is obtained.

Ammonium Compounds.—Platinum, like cobalt, copper, silver, and other metals, yields, with ammonia or with ammonium salts, compounds, which, as in the case of these metals, may be viewed as ammonium compounds, in which one or more molecules of the hydrogen of the ammonium are replaced by platinum. A great many of such platinum compounds have been prepared, and have been divided in no less than twelve classes.

General Character of Platinum Compounds.—All platinum compounds are converted into metallic platinum by ignition in air. Platinic compounds are generally red or yellow, and from their solution caustic potash throws down a yellow precipitate of platinic hydrate, soluble in excess of the precipitant. *Sulphuretted hydrogen* yields a brown precipitate of platinic sulphide, soluble in sulphide of ammonium. *Chloride of potassium or of ammonium* yields a yellow precipitate of the double chloride. The salts are not reduced from their solution to the metallic condition by oxalic acid or stannous chloride, but the latter reduces them to the platinous condition. Ferrous sulphate and formates reduce them only on long continued boiling, but formates reduce them to the metallic state when boiled with them in presence of an excess of alkali.

PALLADIUM.*

Pd=106·6. *Melting point, about* 1,500°. *Specific gravity*, 11·4. *Specific heat*, ·0593.

Occurrence in Nature.—This metal is found in the native state accompanying platinum and gold.

---

[*] So called by Wollaston in 1804, after the then newly discovered planet Pallas.

Properties.—Palladium is dimorphous; it is found crystallised in octahedra and in hexagonal tubes. It resembles platinum in colour, but has a much lower specific gravity, and fuses at a lower temperature than any of the platinum group. It is malleable and ductile, and can be welded. It is soluble in nitric acid, and in warm concentrated sulphuric acid, and in hydrochloric acid in the presence of chlorine or of air. When strongly heated in air it becomes violet in colour owing to slight superficial oxidation, but at a still higher temperature it resumes its original colour.

Its most remarkable property is its attraction for hydrogen, of which it is capable of absorbing 600 times its volume, combining with it chemically; it retains the gas at 100°, but begins to lose it at 130°, and parts with the whole of it on prolonged heating. The hydride which it forms corresponds to the composition Pd_2H. Spongy palladium absorbs 1000 times its volume of hydrogen, but only retains 600 volumes at 100°. The hydrogen compound has a less specific gravity than palladium; it yields up its hydrogen at a high temperature only. Owing to this attraction for hydrogen a piece of palladium held in the flame of a spirit lamp becomes coated with finely divided carbon. Palladium saturated with hydrogen acts as a powerful reducing agent, and will, for example, precipitate mercurous chloride and mercury from a solution of mercuric chloride.

Preparation.—Palladium is separated from solutions containing other metals of the same group by precipitation, as cyanide ($Pd\,Cy_2$), or iodide ($Pd\,I_2$), and from these compounds the metal may be obtained by strongly heating them.

Oxides and Salts.—Palladium forms three oxides—Pd_2O, PdO, and PdO_2. The two latter give off all their oxygen on slowly heating, and form salts known as palladious and palladic salts respectively, the palladious salts being the more stable. Palladious chloride, $Pd\,Cl_2, 2\,H_2O$, may be obtained in red crystals by dissolving the metal in *aqua regia*, and careful evaporation; the palladic chloride is known only in solution. Palladious iodide, $Pd\,I_2$, is precipitated black from a solution of the chloride by a solution of potassium iodide; it is insoluble in water, and forms a most delicate reaction for palladium. Several other salts have been prepared, and many ammonia compounds similar to the platinum compounds are known.

Distinguishing Tests.—Palladious salts yield a black precipitate ($Pd\,I_2$), with a solution of potassium iodide.

IRIDIUM.[*]

Ir=198. *Specific gravity*, 22·38. *Specific heat*, ·0326.

This metal occurs in somewhat larger quantity in the platinum ores, in the form of an alloy with platinum or with osmium (*osmiridium*). It is much less fusible than platinum, and next to osmium and ruthenium it is the least fusible of the group. It is white in colour and is rather brittle. An alloy of platinum and iridium, containing 10 per cent. of iridium, has the elasticity of steel, and is permanent in air. Iridium reduced by hydrogen at a low temperature, oxidises slowly at a red heat, and dissolves in *aqua regia*, but the compact metal is permanent in air and is not acted on by acids or *aqua regia*. Its separation from osmium is based on the volatility of osmium chloride.

It forms several oxides, $Ir\,O$, Ir_2O_3, $Ir\,O_2$, and several salts, corresponding to the two latter, are known.

OSMIUM.[†]

Os=199·2. *Specific gravity*, 22·47. *Specific heat*, ·0311.

This metal occurs alloyed with iridium. It is almost infusible, but slightly volatile, at the highest known temperatures. It is the heaviest of known substances. When finely

---

[*] ἶρις, *the rainbow;* in allusion to its many-coloured salts.

[†] ὀσμή *a smell;* in allusion to the peculiar odour of its volatile oxide.

divided, it takes fire on heating in air and burns to the tetroxide, $Os\,O_4$. It forms several oxides, $Os\,O$, $Os_2\,O_3$, $Os\,O_2$, $Os\,O_3$, and $Os\,O_4$. The trioxide is an acid-forming oxide, but is not known in the free state. The tetroxide is specially characterised by its volatility, and the formation of this compound forms a means of separating osmium from the other platinum metals. This oxide is further characterised by a peculiar odour, and by its dangerous irritant action on the lungs and eyes, and by its highly poisonous nature. A number of salts of the metal are known.

RHODIUM.[*]

Rh=104·4. *Specific gravity*, 12·1. *Specific heat*, 0·0580.

This metal occurs in platinum ores in small quantity. It is white in colour, insoluble in acids and in *aqua regia*, but soluble in the latter when alloyed with much platinum. It is obtained from solutions of the platinum metals after removal of platinum and palladium. It forms three oxides, $Rh\,O$, $Rh_2\,O_3$, and $Rh\,O_2$, of which the salts of the sesquioxide are best known.

RUTHENIUM.[†]

Ru=104·4. *Specific gravity*, 12·26. *Specific heat*, 0·0611.

This metal occurs also in platinum ores and associated with osmiridium. It is hard and brittle, and, after osmium, the most difficultly fusible of the platinum group. It is scarcely attacked by *aqua regia*. The melted metal slowly oxidises in air. It forms no less than six oxides, $Ru\,O$, $Ru_2\,O_3$, $Ru\,O_2$, $Ru\,O_3$, $Ru\,O_4$, and $Ru_2\,O_7$.

GENERAL CHARACTERISTICS OF THE METALS.

As already mentioned in Chap. xiv., the division of the elements into non-metals and metals is not one that can be strictly enforced, for their properties, being a function, apparently, of their atomic weights, more or less merge into each other gradually, without any decided break. Nevertheless, the division is found to be advantageous. The general properties of the various groups should not, however, be taken as characterising in every case members of that group only, but on the whole, as indicating these characters most distinctly. Bearing this in mind, the following generalisations may prove useful.

Occurrence in Nature.—Some metals are found in the free or uncombined state, *native* as it is called; among these are gold, platinum, silver, mercury, copper, bismuth, and (though rarely) iron. Most of these metals are also found in combination (ores). Many are found chiefly combined with oxygen or sulphur; among these are arsenic, manganese, iron, cobalt, nickel, lead, silver, mercury, &c. Many, and especially those whose oxides are strong bases, are found as salts—among these are sodium, potassium, calcium, aluminium, &c.

---

[*] ῥόδον, *a rose*, in allusion to the colour of solutions of its salts.

[†] So called by Osann, in allusion to Russia, where it was first discovered.

A. *Physical Characteristics.*

State of Aggregation.—All the metals are solid at ordinary temperatures, with the exception of mercury. Most of them crystallise in the regular system, and generally in cubes or octahedra.

Lustre.—All metals are possessed of a certain peculiar lustre, which is most aptly described as *metallic lustre;* they exhibit this only in compact masses however, for when in a fine state of division, they are devoid of it, but it may be induced in them, under such circumstances, by pressure between hard surfaces.

Behaviour to Electricity.—They are all, more or less, good conductors of electricity, but differ materially in their conducting power. Silver being the best, is generally taken as the standard (*cf.* Table, p. 46). Copper is also an excellent conductor, and being the cheaper metal, is commonly used for electrical purposes. Iron is a comparatively bad conductor.

Behaviour to Heat.—They are all, more or less, good conductors of heat, and as already pointed out, a remarkable relation exists between their conducting power for heat, and for electricity (see p. 46), so that a metal which is a good conductor of electricity, is equally a good conductor of heat.

All metals are fusible by heat, although here again they differ widely; mercury, for example, fusing at $-39°$, and osmium at 2500°, and all intermediate grades are represented.

Behaviour to Light.—Metals are, ordinarily speaking, in the highest degree opaque to light, some of them, however, as gold and silver, can be obtained in such fine leaves that they become translucent. They are all good reflectors of light when polished, silver being the best.

The *colour* of most metals is greyish-white, some of them, however, have a decided colour—copper is reddish; gold, yellow

Specific Gravity.—As regards specific gravity, they offer also a very wide range; osmium, for example, which is the heaviest, being more than thirty-seven times heavier, bulk for bulk, than lithium, which is the lightest.

In connection with their specific gravity, metals have been divided into two large groups, firstly, those which have a specific gravity below 5, these are called **light metals**; their oxides are heavier than the corresponding metals, and all the members of the group have a strong affinity for oxygen. Most of them have so strong an affinity for oxygen, that they unite with the oxygen of the atmosphere at ordinary temperatures, and cannot, therefore, be used in the arts in the metallic state.

but the compounds of some of them have a very extensive use. This group of light metals consists of the alkali metals, potassium, sodium, lithium, cæsium, rubidium; the metals of the alkaline earths, barium, strontium, and calcium; and the so-called metals of the earths, magnesium, aluminium, and the rarer beryllium, zirconium, thorium, cerium, didyminium, erbium, &c.

Secondly, such as have a specific gravity above 5, are called **heavy metals**; their oxides are lighter than the corresponding metals, and the members of this group have not so strong an affinity for oxygen, and are, therefore, most of them used in the arts. The principal metals belonging to this group are manganese, iron, chromium, cobalt, nickel, zinc, cadmium, copper, lead, bismuth, mercury, antimony, tin, silver, gold, and platinum.

Cohesion.—Some metals, when struck by a hammer, can be beaten out into plates or leaves—they are called *malleable;* others break to pieces when struck—these are called *brittle*. Again, many may be drawn into wire, and these are called *ductile*.

Malleability and ductility do not always go hand in hand; iron, for example, is not very malleable, but is very ductile. Gold is the most malleable of metals; it can be beaten out into leaves so thin that 57 square inches do not weigh more than one grain, and 300,000 would require to be placed on one another to attain to the aggregate thickness of one inch. Platinum is the most ductile of metals. It can be drawn so fine that 3,000 feet of wire would not weigh more than one grain (Wollaston's wire).

Instead of being beaten into plates, some metals are passed between rollers (*rolled*). During rolling and drawing, many metals alter their molecular structure, becoming harder and more brittle, and have to be heated to dull redness to restore their malleability or ductility before the process can be continued.

As regards the *tenacity* of metals, that is, the resistance they offer to being torn asunder, they differ also in this respect considerably—for example, a wire, 2 millimetres in thickness (about $\frac{1}{12}$th of an inch), if of nickel, requires for its rupture a weight of 750 lbs.; if of iron, 500 lbs.; of copper, 274 lbs.; of platinum, 250 lbs.; of silver, 170 lbs.; of gold, 136 lbs.; of zinc, 50 lbs.; of tin, 32 lbs.; and of lead, 24 lbs.

B. *Chemical Characteristics.*

The Metals and Oxygen.—All the metals can be made to unite with oxygen, but they will not all enter into direct combination with it, and they differ further as regards the power with which they retain it when combined. The lower oxides are usually basic, and this basic character, as a general rule, distinguishes these oxides from the corresponding oxides of the non-metals.

According to this varying strength of affinity for oxygen, the metals may be arranged in five groups. Their affinity for this element being measured (*a*) by the action of the metals on water; (*b*) by the behaviour of their oxides to heat.

1. **Potassium, sodium, lithium, cæsium, rubidium, barium, strontium, calcium.**—These metals decompose water at all temperatures, even the lowest, and unite with oxygen at all temperatures, even the highest. Their oxides are very powerful bases, and are soluble in water.

The first five are called the alkali metals; the last three, the metals of the alkaline earths.

2. The most important members of this group are—**magnesium, aluminium, manganese, iron, chromium, nickel, cobalt, zinc, cadmium, uranium, thallium.**—These metals do not decompose water at ordinary temperatures, but require a temperature ranging from 50° to a red heat; but in the presence of a strong mineral acid they decompose it, even at low temperatures. They unite with oxygen, even at the highest temperature, and their oxides cannot be reduced to the metallic state by heat alone. Their lower oxides are bases, but are insoluble in water.

3. The most important members of this group are—**wolfram, titanium, tin, and antimony.**—These metals decompose water only at a red heat, but not at ordinary temperatures, even in the presence of an acid. They unite with oxygen at a red heat. Their oxides are not reduced to the metallic condition by heat.

Their oxides behave as acids to strong alkalies—these metals, therefore, decompose water readily in presence of a strong alkali.

4. **Copper, cadmium, bismuth.**—These metals decompose water only at very high temperatures, and then but feebly, but not at ordinary temperatures, even in the presence of strong acids or alkalies.

They unite with oxygen at a high temperature. Their oxides are not decomposed by heat alone.

. This group, known as the noble or precious metals, includes **mercury, silver, iridium, palladium, platinum, gold.**—These metals do not decompose water under any conditions. Their oxides are decomposed by heat alone.

Metals and the halogens.—Chlorine acts even more violently on the metals than does oxygen. Most of them are easily converted by it into chlorides, some of them under vivid combustion. Bromine and iodine act similarly, but less violently.

Metals and sulphur.—Most metals are capable of entering into direct combination with sulphur when heated with it; some of them burn in its vapour with considerable energy.

Alloys.*—Most metals unite with each other, forming compounds termed alloys, which have a metallic appearance, and which are in their properties generally the intermediate of those of their constituent metals. Most metals may be fused together in every proportion. Some, however, mix only in definite proportions. (Zinc and tin.)

The specific gravity of alloys is generally, but not always, the mean of its components.

The fusing point of alloys is often lower than the melting point of any of the component metals—thus potassium and sodium are both solid at ordinary temperatures, whilst an alloy of the two in atomic proportions is liquid.

Lead fuses at 325°, bismuth at 265°, and tin at 228°, but an alloy, composed of five parts lead, three parts tin, and eight parts bismuth, melts at 98°.

Alloys containing mercury have received the special name of *amalgams.*†

GENERAL CHARACTERISTICS OF SALTS.

We have already learnt (p. 94) that the term, *salt*, is applied to the combination of an acid and a base, that the non-metals yield acid-forming oxides, and that the metals, as a general rule, yield basic oxides.

The metals, iron, manganese, and chromium, are among the more common exceptions to this last rule, since they yield both basic and acid oxides. Salts are divided into *acid* and *basic* salts, according to the preponderance of the acid or basic component, and are called *neutral* when they possess neither acid nor basic properties.

It is the acid component in salts which mainly determines their general physical and chemical characteristics; that is to say, we find those salts most resemble one another in properties which possess the same acid in common.

---

* Old French, *a lai;* Latin, *ad legam*, according to rule or law, a phrase used with reference to the mixing of metals in coinage.—*Skeat.*

† Supposed to be an alchemist's anagram of the Greek word, μάλαγμα, an emollient.

We should classify salts, therefore, according to the acid, and not according to the basic component; this latter plays a secondary *rôle* in more or less modifying the general characteristics due to the former.

State of Aggregation.—Salts are, with few exceptions, *solid* at ordinary temperatures, and are usually, though by no means always, crystalline. Their melting points vary over a considerable range of temperature; the salts of the alkali metals belong to the more fusible, requiring only a gentle red heat.

Specific Gravity.—Their specific gravity naturally varies very greatly, as is also obviously the case with their solutions; the specific gravity of these last varies according to the nature and quantity of the salt dissolved, and the temperature at which the solution is made. In the case of the more common salts, elaborate tables have been constructed, by which it is possible to ascertain the quantity of salt present in a solution from its specific gravity at a given temperature.

Solubility.—With regard to the solubility of salts, this also varies greatly (*cf.*, p. 107). The following general statement, may, however, be made:—The salts of the alkalies, with scarcely any exception, are soluble in water. All neutral nitrates, and, generally speaking, all nitrites, hyposulphites, chlorates, perchlorates, acid phosphates, and acid carbonates, are soluble. All *chlorides* (except silver, thallium, and mercurous chlorides) are soluble. Most *sulphates* (except barium and lead sulphates) are more or less soluble.

The following salts (with the exception of those of the alkali metals and of the sulphides of the alkalies and alkaline earths) are insoluble or difficultly soluble, viz., borates, silicates, arsenates, neutral phosphates, and neutral carbonates, sulphites and sulphides.

Colour.—Most salts are colourless. Some are coloured (*a*) if the acid, (*b*) if the base, or (*c*) if both be coloured. The coloured salts are few in number, and are in consequence easily recognised. Among the more common we may mention—*copper salts* (blue or green), *ferric salts* (reddish-brown), *ferrous salts* and *nickel salts* (green), *chromium salts* (bluish-green), *manganese salts* (pink), *cobalt salts* (red), *salts of chromic acid* (red or yellow), *of manganic acid* (green), *of permanganic acid* (purple red), and *of ferric acid* (red).

APPENDIX.

THERMAL VALUES OF SOME TYPICAL CHEMICAL REACTIONS.

The Thermal changes involved are given in Units of Heat, and represent the effects produced during the formation of one molecule of the substance expressed in grammes.

Substance Formed.	Thermal Change.	Conditions of Formation.
Ozone, O_3 . .	− 17,064	From O_2.
Diamond . .	+ 3,720 about	,, Amorphous Carbon.
Graphite . .	+ 3,412 ,,	,, ,, ,,
Prismatic Sulphur . . .	− 600 ,,	,, Octahedral Sulphur.
Plastic Sulphur	− 90 ,,	,, ,, ,,
Amorphous Phosphorus .	+ 27,373	,, Ordinary Phosphorus.
H_2O	+ 68,357	,, the elements at 18° C.
H_2O	+ 58,069	,, ,, ,, 100° C.
H_2O_2 . . .	− 23,059	,, Water, in dilute solution.
HCl	+ 22,001	Gaseous, from the elements.
HCl + 400 Aq.	+ 39,315	From the elements in presence of 400 molecules of water.
HBr	+ 8,440	,, Liquid Bromine and Hydrogen.
HBr	+ 12,300	,, the elements at 60° C.
HBr + Aq. .	+ 28,376	,, ,, in presence of water.
HI	− 6,036	Gaseous, from the elements.
HI + 400 Aq.	+ 13,171	From the elements in presence of 400 molecules of water.
CO	+ 29,000	,, Oxygen and Amorphous Carbon.
CO_2	+ 67,960	,, CO.
CO_2	+ 96,960	,, Oxygen and Amorphous Carbon.
N_2O	− 17,740	,, the elements.

Substance Formed.	Thermal Change.	Conditions of Formation.
N_2O, O	− 25,410	From N_2O by oxidation.
NO	− 21,575	,, the elements.
NO_2	− 2,005	,, ,,
NO, O	+ 19,570	,, NO by oxidation.
SO_2	+ 71,080	,, Octahedral Sulphur.
SO_2	+ 71,720	,, Prismatic ,,
$SO_2 + Aq$	+ 7,699	Solution of gaseous SO_2 in water.
$SO_2 + Aq$	+ 78,780	Formation of sulphurous acid solution from the elements in the presence of water.
P_2O_5	+ 369,900	From ordinary Phosphorus.
P_2O_5	+ 314,340	,, Amorphous ,,
$SO_2 + Aq, O$	+ 36,634	Formation of H_2SO_4 from aqueous solution of SO_2.
H_2SO_4	+ 192,920	Formation of H_2SO_4 from the elements.
HNO_3	+ 41,510	Direct formation of Acid.
NO, O_2, H	+ 63,085	From NO.
PH_3O_4Aq	+ 305,290	Formation from the elements in presence of water.
$HClO_3, Aq$	+ 23,940	Formation in dilute solution.
$HBrO_3, Aq$	+ 12,420	,, ,, ,,
HIO_3, Aq	+ 55,800	,, ,, ,,
CS_2	− 26,010	From Sulphur and Amorphous Carbon.
KCl	+ 105,610	,, the elements.
$KClO_3$	+ 95,840	Crystallised compound, from the elements.
$KClO_3$	− 9,770	Crystallised ,, from KCl.
KBr	+ 95,310	From the elements.
$KBrO_3$	+ 84,062	Crystallised compound, from the elements.
$KBrO_3$	− 11,248	Crystallised compound, from KBr.
KI	+ 80,130	From the elements.
KIO_3	+ 124,489	Crystallised compound, from the elements.
KIO_3	+ 44,359	Crystallised compound, from KI.
$AgCl$	+ 34,800	From the elements.
$AgBr$	+ 25,618	,, ,,
AgI	+ 18,651	,, ,,
$AgBr$	+ 1,118	,, $AgCl$ and KBr in aqueous solution.
AgI	+ 8,213	,, $AgBr$ and KI in aqueous solution.
AgI	+ 9,331	,, $AgCl$ and KI in aqueous solution.

Specific gravity of solutions of Potash, Soda, and Ammonia.

Per Cent.	K H O.	Na H O.	NH_3.
5	1·036	1·059	0·9790
10	1·077	1·115	0·9593
15	1·124	1·170	·9414
20	1·175	1·225	·9251
25	1·230	1·279	·9106
30	1·288	1·332	·8976
35	1·349	1·384	·8864
40	1·411	1·437	36°/o = ·8844
45	1·475	1·488	...
50	1·539	1·540	...
55	1·604	1·591	...
60	1·667	1·643	...
65	1·729	1·695	...
70	1·790	1·748	...

Specific gravity of solutions of Sulphuric, Nitric, Hydrochloric, Hydrobromic, and Hydriodic Acids respectively.

Per Cent.	H_2SO_4.	HNO_3.	H Cl.	H Br.	H I.
5	1·0320	1·0284	1·0247	1·038	1·045
10	1·0680	1·0587	1·0495	1·077	1·091
15	1·1060	1·0892	1·0750	1·117	1·138
20	1·1440	1·1198	1·1005	1·159	1·187
25	1·1820	1·1526	1·1260	1·204	1·239
30	1·2230	1·1853	1·1510	1·252	1·296
35	1·2640	1·2178	1·1770	1·305	1·361
40	1·3060	1·2673	1·1999	1·365	1·438
45	1·3510	1·3019	42·9°/o=1·212	1·445	1·533
50	1·3980	1·3310	...	1·515	1·650
55	1·4480	1·3650	...	...	52°/o=1·700
60	1·5010	1·3934	...	...	...
65	1·5570	1·4210	...	...	...
70	1·6150	1·4443	...	...	...
75	1·6750	1·4655	...	...	...
80	1·7340	1·4843	...	...	...
85	1·7860	1·5029	...	...	...
90	1·8220	1·5220	...	...	...
95	1·8376	1·5410	...	...	...
100	1·8426	1·5590	...	...	...

Weight of acid contained in 100 *parts of Sulphuric, Nitric, Hydrochloric, Hydrobromic, or Hydriodic Acid Solutions respectively, of various specific gravities at* 15°.

Spec. gr.	H_2SO_4	HNO_3.	HCl.	HBr.	HI.
1·000	0·000	0·000	0·00	0·00	0·00
1·025	4·23	4·47	5·06	3·29	2·77
1·050	7·52	8·65	10·03	6·53	5·56
1·075	10·80	12·70	15·00	9·75	8·19
1·100	14·10	16·80	19·90	12·88	10·95
1·125	17·30	20·80	24·80	15·95	13·62
1·150	20·56	24·60	28·30	18·93	16·22
1·175	23·83	28·42	34·70	21·86	18·75
1·200	27·10	32·25	40·03	24·56	21·25
1·225	30·24	36·10	1·212 = 42·9	27·18	23·66
1·250	33·18	39·88	...	29·79	25·96
1·275	36·25	43·50	...	32·07	28·16
1·300	39·20	47·37	...	34·53	30·30
1·325	42·20	51·37	...	36·66	32·24
1·350	44·86	55·70	...	38·75	33·74
1·375	47·44	60·12	...	40·62	35·91
1·400	50·12	64·93	...	42·18	37·75
1·425	52·88	70·38	...	43·75	39·16
1·450	55·12	77·26	...	45·35	40·63
1·475	57·55	84·36	...	47·14	41·94
1·500	59·77	92·26	...	49·93	43·27
1·525	62·03	98·33	...	1·515 = 50	44·58
1·550	64·65	1·530 = 100	...	...	45·72
1·575	66·56	...	...	...	46·79
1·600	68·83	...	...	...	47·87
1·625	70·84	...	...	...	48·92
1·650	73·02	...	...	...	50·00
1·675	74·97	...	...	...	51·00
1·700	77·11	...	...	...	52·00
1·725	78·70	...	...	...	...
1·750	81·39	...	...	...	...
1·775	84·33	...	...	...	...
1·800	86·81	...	...	...	...
1·825	92·31	...	...	...	..
1·842	100·00	...	...	...	...

Conversion of degrees of **Twaddell** *or* **Beaumé** *hydrometers into specific gravity.*

If T = degree Twaddell, then

$$\text{Specific gravity required} = \frac{T \times 5 + 1000}{1000}.$$

If B = degree Beaumé, then for liquids heavier than water,

$$\text{Specific gravity required} = \frac{144}{144 - B}$$

And for liquids lighter than water,

$$\text{Specific gravity required} = \frac{144}{144 + B}.$$

FINIS.

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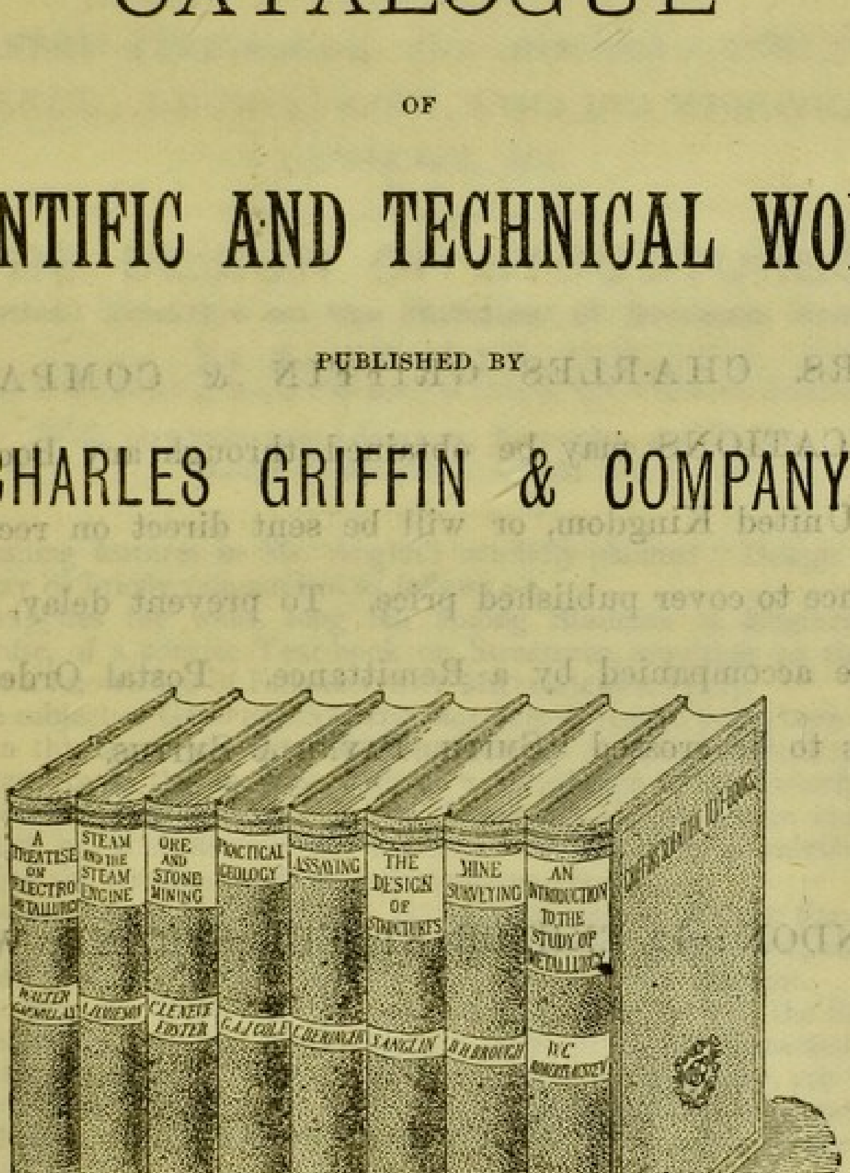

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