A manual of chemistry

Physical and inorganic chemistry

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Introduction

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A

MANUAL OF CHEMISTRY.

PHYSICAL AND INORGANIC.

INTRODUCTION.

THE Science of Chemistry has for its object the study of the nature and properties of the materials which enter into the composition of the earth, the sea, and the air, and of the various organised or living beings which inhabit them.

In ordinary scientific speech the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical*, which are not attended by such consequences. Changes of decomposition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and the attractive forces, whose laws and effects lie within the province of Physics.

Nearly all the objects presented by the visible world are of a compound nature, and capable of being resolved into simpler forms of matter. Thus, a piece of limestone or marble, by the application of a red heat, is decomposed into quicklime and a gaseous body, carbon dioxide. Both lime and carbon dioxide are in their turn susceptible of decomposition—though not by the action of heat alone—the former into calcium and oxygen, the latter into carbon and oxygen. Beyond this second step of decomposition the efforts of Chemistry have hitherto been found to fail; and the three bodies calcium, carbon, and oxygen, having resisted all attempts to resolve them into simpler forms of matter, are admitted into the list of *elements;* not from an absolute belief in their real oneness of nature, but from the absence of any evidence that they contain more than one description of matter.

The elementary bodies, at present recognised, are sixty-seven in number, and about fifty of them belong to the class of *metals.* Several of these are of recent discovery, and are as yet very imperfectly known. The distinction between metals and non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, the two classes not being separated by any exact line of demarcation.

The names of the elements are given in the following table. Opposite to them in the third column are placed certain numbers, which express the proportions in which they combine together, or simple multiples of those proportions; these numbers, for reasons which will be afterwards explained, are called Atomic or Indivisible Weights. In the second column are placed symbols by which these weights are denoted; these symbols are formed of the first letters of the Latin names of the elements, a second letter being added when the names of two or more elements begin with the same letter.

The names of the most important elements are distinguished by the largest and most conspicuous type; those next in importance, by small capitals; while the names of elements which are of rare occurrence, or of which our knowledge is still imperfect, are printed in ordinary type. The names with an asterisk are those of Non-metallic Elements, the others are names of Metals.

Table of Elementary Bodies with their Symbols and Atomic Weights.

Name.	Symbol.	Atomic Weight.	Name.	Symbol	Atomic Weight.
ALUMINIUM	Al	27·3	Nickel	Ni	58·6
Antimony (Stibium)	Sb	122	Niobium	Nb	94
Arsenic	As	74·9	**NITROGEN***	N	14·01
Barium	Ba	136·8	Osmium	Os	198·6
Beryllium	Be	9	**OXYGEN***	O	15·96
Bismuth	Bi	210	Palladium	Pd	106·2
Boron*	B	11	**PHOSPHORUS***	P	30·96
BROMINE*	Br	79·75	**PLATINUM**	Pt	196·7
Cadmium	Cd	111·6	**POTASSIUM** (Kalium)	K	39·04
Cæsium	Cs	133	Rhodium	Rh	104·1
CALCIUM	Ca	39·9	Rubidium	Rb	85·2
CARBON*	C	11·97	Ruthenium	Ru	103·5
Cerium	Ce	141·2	Scandium	Sc	44·9
CHLORINE*	Cl	35·37	Selenium*	Se	78
Chromium	Cr	52·4	**SILICON**	Si	28
Cobalt	Co	58·6	**SILVER** (Argentum)	Ag	107·66
COPPER (Cuprum)	Cu	63	**SODIUM** (Natrium)	Na	23
Didymium	D	146·6	Strontium	Sr	87·2
Erbium	E	166	**SULPHUR***	S	31·98
FLUORINE*	F	19·1	Tantalum	Ta	182
Gallium	Ga	69·8	Tellurium*	Te	128
Gold (Aurum)	Au	196·2	Terbium	Tb	148
HYDROGEN*	H	1	Thallium	Tl	203·6
Indium	In	113·4	Thorium	Th	231·5
IODINE*	I	126·53	**TIN** (Stannum)	Sn	117·8
Iridium	Ir	196·7	Titanium	Ti	48
IRON (Ferrum)	Fe	55·9	Tungsten, or Wolfram	W	184
Lanthanum	La	139	Uranium	U	240
LEAD (Plumbum)	Pb	206·4	Vanadium	V	51·2
Lithium	Li	7	Ytterbium	Yb	172·5?
Magnesium	Mg	23·94	Yttrium	Y	89
MANGANESE	Mn	54·8	**ZINC**	Zn	64·9
MERCURY (Hydrargyrum)	Hg	199·8	Zirconium	Zr	90
Molybdenum	Mo	95·6			

It must be distinctly understood that the atomic or combining weights assigned to the elements are merely relative. The number 1 assigned to hydrogen may represent a grain, ounce, pound, gram, kilogram, &c., and the numbers assigned to the other elements will then represent so many grains, ounces, pounds, grams, kilograms, &c. Hydrogen is taken as the unit of the scale, because its combining weight is smaller than that of any other element; but this is merely a matter of convenience; in the older tables of atomic weights that of oxygen was assumed as 100, that of carbon being then 75, that of hydrogen 6·25, &c., &c.

By the combination of the elements in various proportions, and in groups of two, three, or larger numbers, all compound bodies are produced. And here it is important to state clearly the characters which distinguish true chemical combination from mechanical mixture, and from that kind of adhesion which gives rise to the solution of a solid in a liquid. Bodies may be mixed together in any proportion whatever, the mixture always exhibiting properties intermediate between those of its constituents, and in regular gradation, according to the quantity of each that may be present, as may be seen in the fusion together of metals to form alloys, in the mixture of water with alcohol, of alcohol with ether, and of different oils one with the other. A solid body may also be dissolved in a liquid—salt or sugar in water, for example—in any proportion up to a certain limit, the solution likewise exhibiting a regular gradation of physical properties, according to the quantity of the solid taken up. But a true chemical compound exhibits properties totally different from those of either of its constituent elements, and the proportion of these constituents which form that particular compound admits of no variation whatever. Water, for example, is composed of two elements, oxygen and hydrogen, which, when separated from one another, appear as colourless gases, differing widely in their properties one from the other, and from water in the state of vapour; moreover, water, whether obtained from natural sources, or formed by direct combination of its elements, always contains in 100 parts by weight, 88·9 parts of oxygen and 11·1 of hydrogen. Common salt, to take another example, is a compound of chlorine and sodium, the former of which, in the separate state, is a yellowish-green gas, the latter a yellowish-white highly lustrous metal, capable of burning in the air, and decomposing water; moreover, from whatever part of the world the salt may be obtained, 100 parts of it invariably contain 39·6 parts of sodium and 60·4 parts of chlorine. Further, when two or more compounds are formed of the same elements, there is no gradual blending of one into the other, as in the case of mixtures, but each compound is sharply defined, and separated, as it were, from the others by an impassable gulf, exhibiting properties distinct from those of the others, and of the elements themselves in the separate state. Thus, there are two compounds of carbon and oxygen, one of which, containing 3 parts by weight of carbon with 4 of oxygen, is an inflammable gas, lighter than atmospheric air, and not absorbed by solution of potash; while the other, which contains 3 parts of carbon and 8 of oxygen, is non-inflammable, heavier than air, and easily absorbed by potash.

Oxygen is the most widely diffused of all the elementary bodies. It is under ordinary circumstances a gas, and, mixed with nitrogen, constitutes the air which we breathe. In combination with hydrogen it forms water. In the pure state it is a colourless inodorous gas, in which inflammable bodies, such as wood, oil, sulphur, &c., burn much more rapidly than in common air.

Nitrogen, the other constituent of the air, is also a colourless gas, non-inflammable, and differing from oxygen in not being capable of maintaining the combustion of other bodies, so that a lighted taper immersed in it is immediately extinguished.

Hydrogen, the other constituent of water, is in the free state also a gas, and is the lightest of all known bodies. In presence of oxygen or common air, it is very inflammable, and burns with a light blue flame, producing water.

Carbon is a constituent of all vegetable and animal substances, existing therein in combination either with hydrogen alone, or with hydrogen and oxygen, or with hydrogen, oxygen, and nitrogen. When separated from these elements, it is for the most part a black solid body, well known under the names of charcoal, coke, lamp-black, and plumbago, or black-lead. It occurs also naturally in the pure state, forming transparent crystals known as diamond.

Chlorine, Bromine, and Iodine exist in sea-water (hence called *Halogen-elements*, from ἅλς, the sea), in combination chiefly with sodium. Chlorine in the free state is a yellowish-green gas, bromine a red liquid, iodine a greyish-black crystalline solid. Of these elements, chlorine is by far the most abundant, its compound with sodium forming common sea-salt. Fluorine is an element closely allied in its chemical relations to the three last mentioned. It is not known in the free state, but in combination with calcium it constitutes the crystallised mineral called fluorspar.

Sulphur, a well-known substance, occurs in the free state in volcanic districts, and abundantly in various parts of the world in combination with iron, copper, lead, and other metals, forming compounds called *sulphides*. Selenium and Tellurium are rare elements, allied to sulphur, and likewise found in combination with metals.

Phosphorus, in the free state, is a highly inflammable solid body, which burns rapidly in contact with the air, being converted, by combination with oxygen, into *phosphoric acid*, a compound which, in combination with calcium, occurs very abundantly in nature, forming the minerals called phosphorite and apatite, and is the chief mineral constituent of the bones of animals. Arsenic, sometimes regarded as a metal, is an element closely allied in its chemical relations to phosphorus, and occurring in nature in combination with oxygen, sulphur, and various metals.

Silicon is a very abundant and important element, not occurring in nature in the free state, but forming, in combination with oxygen, the mineral called *silica*, which in the form of quartz, flint, and sandstone, and as a constituent of granite, gneiss, and other ancient rocks, forms a very large portion of the crust of the earth. Boron, an element analogous in many of its properties to silicon, occurs naturally in combination with oxygen, forming boric or boracic acid, which is a constituent of several minerals, and occurs somewhat abundantly in solution in certain natural waters.

Of the fifty-four metals, seven only were known in ancient times, viz., iron, copper, lead, tin, mercury, silver, and gold; of these, by far the most abundant and important is iron. Of the metals more recently discovered, the most abundant are sodium, potassium, calcium, and aluminium. Sodium, as already observed, forms, in combination with chlorine, the chief saline constituent of sea-water. Potassium, which resembles it in many respects, exists also in the sea, and is a constituent of all plants. Calcium is the metallic constituent of limestone, and aluminium of clay.

General Laws of Chemical Combination.—Chemical Nomenclature and Notation.—The compounds formed by the union of oxygen with other bodies bear the general name of oxides. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations the oxides of potassium, sodium, silver, or lead: these are denominated alkaline or basic oxides. The oxides of the second group have properties opposed to those of the bodies mentioned; the oxides of sulphur and phosphorus may be taken as typical representatives of the class; they are called acid oxides, and are capable of uniting with the basic oxides, and forming compounds called salts. Thus, when the oxide of sulphur, called sulphuric oxide, is passed in the state of vapour over heated barium oxide, combination takes place, attended with vivid incandescence, and a salt called barium sulphate is produced, containing all the elements of the two original bodies, namely, barium, sulphur, and oxygen.

Among salts there is a particular group, namely, the hydrogen salts, containing the elements of an acid oxide and water (hydrogen oxide), which are especially distinguished as acids, because many of them possess in an eminent degree the properties to which the term acid is generally applied, such as a sour taste, corrosive action, solubility in water, and the power of reddening certain blue vegetable colours. A characteristic property of these acids, or hydrogen salts, is their power of exchanging their hydrogen for a metal presented to them in the free state, or in the form of oxide. Thus, sulphuric acid, which contains sulphur, oxygen, and hydrogen, readily dissolves metallic zinc, the metal taking the place of the hydrogen, which is evolved as gas, and forming a salt containing sulphur, oxygen, and zinc; in fact, a *zinc sulphate*, produced from a *hydrogen sulphate* by substitution of zinc for hydrogen. The same substitution and formation of zinc sulphate take place when zinc oxide is brought into contact with sulphuric acid; but in this case the hydrogen, instead of being evolved as gas, remains combined with the oxygen derived from the zinc oxide, forming water.

A series of oxides containing quantities of oxygen in the proportion of the numbers 1, 2, 3, united with a constant quantity of another element, are distinguished as *monoxide*, *dioxide*, and *trioxide* respectively, the Greek numerals indicating the several degrees of oxidation. A compound intermediate between a monoxide and a dioxide is called a *sesquioxide*, *e.g.*:—

	Chromium.		Oxygen.
Chromium monoxide	52·4	+	16
Chromium sesquioxide	52·4	+	24
Chromium dioxide	52·4	+	32
Chromium trioxide	52·4	+	48

When a metal forms two basic or salifiable oxides, they are distinguished by adjectival terms, ending in *ous* for the lower, and *ic* for the higher degree of oxidation, *e.g.*:—

	Iron.		Oxygen.
Iron monoxide, or Ferrous oxide . .	56	+	16
Iron sesquioxide, or Ferric oxide . .	56	+	24

The salts resulting from the action of acids on these oxides are also distinguished as ferrous and ferric salts respectively.

Acid oxides of the same element, sulphur for example, are also distinguished by the terminations *ous* and *ic*, applied as above; their acids, or hydrogen salts, receive corresponding names; and the salts formed from these acids are distinguished by names ending in *ite* and *ate* respectively. Thus, for the oxides and salts of sulphur:—

	Sulphur.		Oxygen.		
Sulphurous oxide	32	+	32		
					Hydrogen.
Hydrogen sulphite, or Sulphurous acid	32	+	48	+	2
					Lead.
Lead sulphite	32	+	48	+	206·4

	Sulphur.		Oxygen.		
Sulphuric oxide	32	+	48		
					Hydrogen.
Hydrogen sulphate, or Sulphuric acid	32	+	64	+	2
					Lead.
Lead sulphate	32	+	64	+	206·4

The acids above spoken of are oxygen-acids; and formerly it was supposed that all acids contained oxygen—that element being, indeed, regarded as the acidifying principle. At present, however, we are acquainted with many bodies which possess all the characters above specified as belonging to an acid, and yet do not contain oxygen. For example, hydrochloric acid (formerly called muriatic acid, or spirit of salt)—which is a hydrogen chloride or compound of hydrogen and chlorine—is intensely sour and corrosive; reddens litmus strongly; dissolves zinc, which drives out the hydrogen and takes its place in combination with the chlorine, forming zinc chloride; and dissolves most metallic oxides, exchanging its hydrogen for the metal, and forming a metallic chloride and water.

Bromine, iodine, and fluorine, also form, with hydrogen, acid compounds analogous in every respect to hydrochloric acid.

Compounds of chlorine, bromine, iodine, fluorine, sulphur, selenium, phosphorus, &c., with hydrogen and metals, are grouped, like the oxygen-compounds, by names ending in *ide:* thus we speak of zinc chloride, calcium fluoride, hydrogen sulphide, copper phosphide, &c. The numerical prefixes, *mono*, *di*, *tri*, &c., as also the terminations *ous* and *ic*, are applied to these compounds in the same manner as to the oxides, thus—

	Hydrogen.		Bromine.
Hydrogen bromide	1	+	80
	Potassium.		Sulphur.
Potassium monosulphide	78	+	32
Potassium disulphide	78	+	64
Potassium trisulphide	78	+	96
Potassium tetrasulphide	78	+	128
Potassium pentasulphide	78	+	160
	Iron.		Chlorine.
Ferrous chloride	56	+	71
Ferric chloride	56	+	106·5

	Tin.		Sulphur.
Stannous sulphide	117·8	+	64
Stannic sulphide	117·8	+	128

The Latin prefixes *uni*, *bi*, *ter*, *quadro*, &c., are often used nstead of the corresponding Greek prefixes; there is no very exact rule respecting their use; but, generally speaking, it is best to employ a Greek or Latin prefix, according as the word before which t is placed is of Greek or Latin origin. Thus, *di*oxide corresponds with *bi*sulphide; on the whole, however, the Greek prefixes are most generally employed.

The composition of these oxides and sulphides affords an illustration of a law which holds good in a large number of instances of chemical combination, viz., that *when two bodies*, A *and* B, *are capable of uniting in several proportions, the several quantities of* B *which combine with a given or constant quantity of* A *stand to one another in very simple ratios.* Thus, the several quantities of sulphur which unite with a given quantity (78 parts) of potassium are to one another as the numbers

1, 2, 3, 4, 5;

and the quantities of oxygen which unite with a given quantity of chromium are as the numbers,

1, $1\frac{1}{2}$, 2, 3,
or 2, 3, 4, 6.

It must be especially observed that no compounds are known intermediate in composition between those which are represented by these numbers. There is no oxide of chromium containing $1\frac{1}{4}$ or $1\frac{5}{8}$ or $2\frac{7}{8}$ times as much oxygen as the lowest; no sulphide of potassium the quantity of sulphur in which is expressed by any fractional multiple of the lowest. The quantities of the one element which can unite with a constant quantity of the other, increase, not continuously, but by successive and well-defined steps or increments, standing to one another, for the most part, in simple numerical ratios.

This is called the "Law of Multiples." The observation of it has led to the idea that the elementary bodies are composed of ultimate or indivisible particles or **atoms**, each having a constant weight peculiar to itself (the atomic weights given in the table on page 3), and that combination between two elements takes place by the juxtaposition of these atoms. A collection of elementary atoms united together to form a compound constitutes a **molecule**, the weight of which is equal to the sum of the weights of its component atoms. Thus an atom of chlorine weighing 35·4 unites with an atom of hydrogen weighing 1, to form a molecule of hydrogen chloride weighing 36·4. An atom of oxygen weighing 16 unites with 2 atoms of hydrogen, each weighing 1, to form a molecule of water, weighing $16 + 2 . 1 = 18$. An atom of oxygen, weighing 16, unites with an atom of lead, weighing 206·4, to form a molecule of lead oxide, weighing 222·4. Two atoms of potassium, each weighing 39, unite with 1, 2, 3, 4, and 5 atoms of sulphur, each weighing 32, to form the several sulphides enumerated on page 9.

These combinations are represented symbolically by the juxtaposition of the symbols of the elementary atoms given in the table already referred to; thus the molecule of hydrogen chloride, composed of 1 atom of hydrogen and 1 atom of chlorine, is represented by the symbol or formula HCl; that of water (2 atoms of hydrogen and 1 atom of oxygen), by HHO, or more shortly H_2O. In like manner the different oxides, sulphides, acids and salts above enumerated, are represented symbolically as follows:—

Chromium monoxide . . .	CrO	
Chromium sesquioxide . . .	CrCrOOO	or Cr_2O_3
Chromium dioxide . . .	CrOO	or $Cr\ O_2$
Chromium trioxide . . .	CrOOO	or $Cr\ O_3$
Sulphurous oxide	SOO	or SO_2
Hydrogen sulphite or Sulphurous acid	SOOOHH	or SO_3H_2
Lead sulphite	SOOOPb	or SO_3Pb
Potassium monosulphide . .	KKS	or K_2S
Potassium disulphide . . .	KKSS	or K_2S
Potassium trisulphide . . .	KKSSS	or K_2S_3
Potassium tetrasulphide . .	KKSSSS	or K_2S_4
Potassium pentasulphide . .	KKSSSSS	or K_2S_5

A group of two or more atoms of the same element is denoted by placing a numeral either before the symbol, or, as in the preceding examples, a small numeral to the right of the symbol, and either above or below the line; thus OOO may be abbreviated into 3O, or O^3, or O_3.

The multiplication of a group of dissimilar atoms is denoted by placing a numeral to the left of the group of symbols, or by enclosing them in brackets, and placing a small numeral to the right: thus, 3HCl or $(HCl)_3$ denotes 3 molecules of hydrogen chloride; $2H_2SO_4$ denotes 2 molecules of hydrogen sulphate.

The combination of two groups or molecules is denoted by placing their symbols in juxtaposition, with a comma between them: thus ZnO,SO_3 denotes a compound of zinc oxide with sulphur trioxide; K_2O,H_2O, a compound of potassium oxide with hydrogen oxide or water. Sometimes the sign + is used instead of the comma. To express the multiplication of such a group, the whole is enclosed in brackets, and a numeral placed on the left; *e.g.*, $2(ZnO,SO_3)$; $3(K_2O,H_2O)$, &c. If the brackets were omitted, the numeral would affect only the symbols to the left of the comma; thus $3K_2O,H_2O$ signifies 3 potassium oxide and 1 water, not 3 potassium oxide and 3 water.*

Equivalents.—It has been already stated that elements can replace one another in combination; thus, when hydrogen chloride is placed in contact with zinc, the zinc dissolves and enters into combination with the chlorine, while a quantity of hydrogen is evolved as gas. Now this substitution of zinc for hydrogen always takes place in definite proportion by weight, 32·5 parts of zinc being dissolved for every 1 part of hydrogen expelled. In like manner when potassium is thrown into water, hydrogen is evolved and the potassium dissolves, 39 parts of the metal dissolving for every 1 part of hydrogen given off. Again, if silver be dissolved in nitric acid, and metallic mercury immersed in the solution, the mercury will be dissolved and

* The neglect of this distinction often leads to considerable confusion in chemical notation.

will displace the silver, which will be separated in the metallic state; and for every 100 parts of mercury dissolved 108 parts of silver will be thrown down. In like manner copper will displace the mercury in the proportion of 31·5 parts of copper to 100 of mercury, and iron will displace the copper in the proportion of 28 parts of iron to 31·5 parts of copper.

These are particular cases of the general law, that, *when one element takes the place of another in combination, the substitution or replacement always takes place in fixed or definite proportions.* The relative quantities of different elements which thus replace one another, are called chemical equivalents or equivalent numbers; they are either identical with the atomic weights, or simple multiples, or submultiples of them. For example, in the substitution of potassium for hydrogen, and of copper for mercury, and of iron for copper, the equivalents are to one another in the same proportion as the atomic weights, as may be seen by comparing the numbers just given with those in the table on page 3. In the substitution of zinc for hydrogen, on the other hand, the quantity of zinc which takes the place of 1 part of hydrogen is only half the atomic weight; similarly in the substitution of mercury for silver.

All chemical reactions consist either in the direct addition or separation of elements, or in substitutions like those just noticed, the latter being by far the most frequent form of chemical change.

Chemical Equations.—Chemical reactions may be represented symbolically in the form of equations, the symbols of the reacting substances being placed on the left hand, and those of the new substances resulting from the change, on the right: for example—

1. Resolution of mercuric oxide by heat into mercury and oxygen—

$$HgO = Hg + O.$$

2. Resolution of manganese dioxide by heat into manganoso-manganic oxide and oxygen—

$$3MnO_2 = Mn_3O_4 + O_2.$$

3. Action of zinc on hydrogen chloride, producing zinc chloride and free hydrogen—

$$2HCl + Zn = ZnCl_2 + H_2.$$

4. Action of zinc on hydrogen sulphate, producing zinc sulphate and hydrogen—

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$

5. Action of zinc oxide on hydrogen chloride or sulphate, producing zinc chloride or sulphate and water—

$$2HCl + ZnO = ZnCl_2 + H_2O,$$

and

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

It need scarcely be observed that the test of correctness of such an equation is, that the number of atoms of each element on one side should be equal to the number of atoms of the same element on the other side.

Any such symbolical equation may be converted into a numerical equation, by substituting for each of the chemical symbols its numerical value from the table of atomic weights.

The laws of chemical action and their expression by symbols and equations will receive abundant illustration in the special descriptions which follow; their general consideration will also be more fully developed in a subsequent part of the work.

Before proceeding with the detailed description of the several elements and their compounds, it is desirable to give a short sketch of certain branches of Physical Science, viz., the mechanical constitution of gases, and the chief phenomena of heat, light, electricity, and magnetism, the partial study of which greatly facilitates the understanding of chemical reactions.