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Manuals of Pure and Applied Chemistry

SYMBOLS AND FORMULÆ
IN CHEMISTRY

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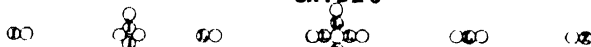
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(Atomic Symbols)
 BY
John Dalton, D.C.L. F.R.S. &c.
 EXPLANATORY OF A LECTURE
given by him
 to the Members of the
Manchester Mechanics Institution
 19th October, 1835.

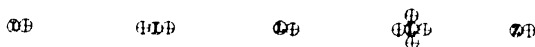
ELEMENTS

Hydrogen	○	Oxygen	○	Hydro	①	Chlorine	③
Carbon	○	Phosphorus	⊕	Sulphur	⊕	Lead	④
Zinc	②	Iron	①	Tin	①	Copper	④

OXIDES



SULPHURETS.



COMPOUNDS.

Binary		Quaternary	
Water	○ ○	Sulphuric acid	
Nitrous gas	○ ○	Binclifiant gas	
Carbonic oxide	● ○	Pyroxylic spirit	
Sulphuretted hydrogen	○ ○	Quinquenary.	
Phosphuretted hydrogen	○ ○	Ammonia	
Elephant gas	● ○	Nitrous acid	
Cyanogen	● ○		
Ternary		Sexenary	
Oxide of hydrogen	○ ○ ○	Prussic acid	
Sulphurous acid	○ ○ ○	Alcohol	
Nitric acid	○ ○ ○	Pyroxylic spirit	
Carbonic acid	○ ○ ○	Septenary	
Phosphoric acid	○ ○ ○	Nitric acid	
Nitrous vapour	○ ○ ○		
Carbonated hydrogen	○ ○ ○		
Prussic acid	○ ○ ○		
Bicarbonated hydrogen	○ ○ ○		
Tin	○ ○ ○	Decenary.	

SYMBOLS AND FORMULÆ IN CHEMISTRY

An Historical Study

BY

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1928

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PREFACE

This book has arisen out of a two-fold interest: an antiquarian interest in the past, and a scientific interest in the present. Symbols in chemistry, like fashions in dress, have changed greatly from age to age; and in the pages of this volume a parade is arranged for all who care to see them.

Some of these creations have not met the light for many a year, and make a quaint and even amusing display; others, which looked very well when new, are rather worn and out of date; whilst still others—the modern ones—are somewhat daring and difficult, and calculated to shock the propriety of the steady-going chemist who is getting on in years. Nevertheless, in the newest fashions some primitive ideas seem to be revived to give point to the old adage that there is nothing new under the sun. So here they all are, even the latest of them, borrowed from the pages of current journals to bring the pageant down to the present day.

We have made free use of the library of the Royal Technical College, and gratefully acknowledge the help and interest of Mr. Wm. G. Burrell, M.A., the Librarian. We are indebted to a number of standard works, particularly that of Mr. Pattison Muir on *A History of Chemical Theories and Laws*, as well as to Mr. G. F. Rodwell's *The Birth of Chemistry*. The resources of the Glasgow University Library have also been made available through the kindness of Mr. Wilson Steel, Sub-librarian, to whom our thanks are due; we wish also to thank Mr. Harvey P. Arthur for drawing our attention to an article on Hindu symbols.

The extensive account of the work of Berzelius is due to our good fortune in securing a copy of that author's *Théorie des Proportions chimiques*.

R. M. C.
J. A. C.

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SYMBOLS AND FORMULÆ IN CHEMISTRY

CHAPTER I

The Beginnings of Symbolism

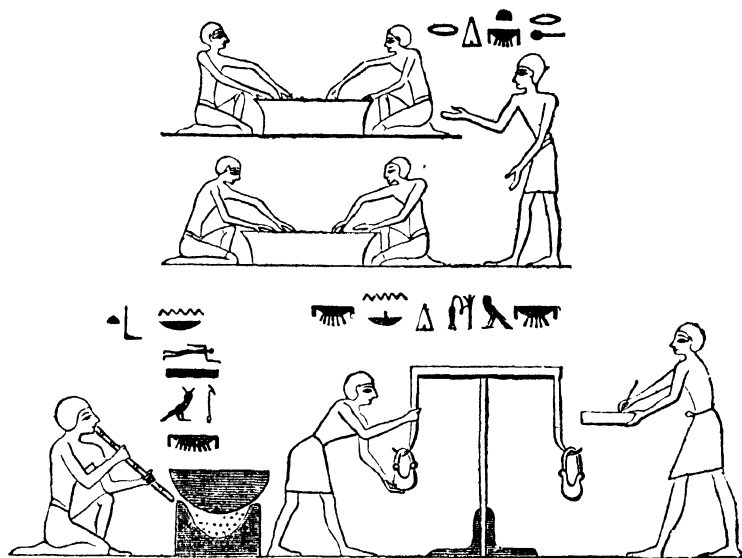
Symbolism has its roots deep in human nature. The desire for self-expression is fundamental, and symbols are needed to record experiences which would otherwise be forgotten. The primitive savage made crude drawings of animals on the walls of his rock dwelling, before he conceived the idea of recording speech and thought by symbols. Writing was at first pictorial as well as symbolic; that is to say it represented familiar objects and ideas by drawings which could afterwards be used to recall those objects or ideas. As a rule, in the development of writing, pictures became conventionalized and transformed into symbols, or gave place to simpler signs which were the letters of the alphabet. In one language, Chinese, however, the pictures have remained in the writing, and thus visibly represent material objects. The Chinese characters, e.g. for sun and moon, for mountain and tree, were originally drawings of these objects, and they still preserve the signs of their origin. Characters, also, are put together in Chinese to represent more complex ideas; thus two trees together represent a forest, and trees with the sun seen through them stand for the east.

In ancient times, then, pictorial symbols for material objects were in general use; therefore symbols for chemical substances may be looked for in early literature.

Alchemy was practised in ancient Chaldea; and, although no trace of Chaldean symbols can be found, the influence of Chaldean thought is seen in Alchemy. Thus the Chaldeans regarded the number 7, representing one-fourth of the days in a lunar month,

2 SYMBOLS AND FORMULÆ IN CHEMISTRY

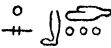
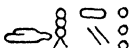
as sacred and mystical. Seven planets in the sky, seven gods in heaven, seven gods on earth, seven devils, seven coloured stones of ascent to their temples, seven metals, or at any rate five metals: gold, silver, copper, lead, and tin, with probably marble and alabaster. So it was from Chaldea that the mediæval alchemists learned of seven



Design from an Early Egyptian Tomb, showing the Washing, Refining, and Weighing of Gold

metals, to which they applied the symbols of the sun, moon, and five planets.

It is in ancient Egyptian lore, however, that primitive symbolism first appears. Thus the figure  containing a cobra, symbolizes whiteness; whilst  which is a modification of the former, stands for silver. The slightly different symbol  represents gold: and this can be found with other symbols in the accompanying drawing, which is an ancient Egyptian representation of the washing, refining, and weighing of the precious metal. The symbol  was used for the sun by the ancient Egyptians; but it was not used for gold till a later time. The single wavy line  was the letter N, but a triple line , which evidently suggested waves, stood for water. Sometimes the Egyptian symbols for material substances are really words composed of ancient letters.

Thus the symbol  has been found to spell the word *chesbet*, which stands for blue enamel; whilst the symbol  spells *teht*, which stands for lead; the three small circles common to both signs signify a mineral substance.

When we turn to ancient Greece we find philosophies which were accompanied by symbolism. The natural philosophy of the Greeks is divisible into two schools, which may be described as materialistic and idealistic. The materialistic school comprised the teaching of Democritus (c. 460–360 B.C.) and Epicurus (341–270 B.C.), which was embodied in the poem *De Rerum Natura* by Lucretius (98–54 B.C.). Following the sages of India, these philosophers taught that the ultimate parts of matter were solid, eternal, and unchangeable atoms, perpetually moving in the void. If these atoms had parts at all, such parts could not exist by themselves; they were conceived of only to bridge the gulf between the atom and the void—between something and nothing. All existences, all forms of life and thought, as well as all the phenomena of lifeless matter, were reducible to the atoms and their motions.

No symbols of these ancient atoms can be shown; the most we know about them is that they were sometimes provided with hooks by which they could become attached to one another, and so built up into the structure of matter.

It will hardly be supposed that such philosophy suffices to set forth the totality of existence; yet it undoubtedly forms a valuable basis for the science of chemistry; and it is easy to understand that if experimental support had been found for it, it might have become firmly established as a foundation of the science. Apart from such support, however, the theory was liable to encounter and be displaced by metaphysical speculation regarding the nature of things.

Plato (427–344 B.C.) represents the idealistic school of ancient philosophy. To Plato Ideas were the great realities; phenomena were fleeting. Thus the classification of material things originated in the mind, and was projected therefrom into the world without.

Democritus spoke of different kinds of atoms; Plato of different elements. Yet the elements of Plato were not composed of the atoms of Democritus. They were first of all ideas; and then they became qualities of things rather than things themselves.

Plato's elements were four. First *Fire*, which made things visible, and then *Earth*, which made solid things tangible; afterwards *Air*

and *Water*, "set between fire and earth . . . so that fire is to air as air is to water; and as air is to water, water is to earth".*

Plato symbolized his elements by solid, geometrical forms. Thus Earth was symbolized by a cube, Water by a regular icosahedron, i.e. a solid figure bounded by twenty equilateral triangles, like the facets of a diamond, Air by a regular octahedron, and Fire by a regular tetrahedron. The first two of these figures were supposed to represent the stability of earth, and the mobility of water; whilst air and fire, being more nimble and keen than water and earth, were represented by figures with fewer sides and therefore sharper solid angles. These symbols are by no means chemical symbols; they are the fancies of a philosopher, which have no scientific utility. The Chinese Buddhists symbolized the four elements similarly. Thus a square stood for earth, a circle for water, a triangle for fire, and a crescent for air.

The four elements, however, which were adopted from Plato by his pupil Aristotle, may be supposed to have some scientific value, because earth, water, and air stand for solid, liquid, and gas, whilst fire typifies energy. Yet they describe the changing properties and forms of things, and do not serve to classify things apart from their forms. For when Earth, for example, is said to be the element of dryness and coldness so that all dry and cold things contain it, Earth is not a chemical element at all but only an abstraction. The atomic theory of Democritus was a scientific concept, although it was unsupported by experiment; the elemental theory of Plato was a philosopher's dream, beautiful in its far-reaching thought, but misleading if taken for science.

It has been said that the view-points of Democritus and Plato regarding the world were opposite and corresponded respectively with materialistic and idealistic philosophy. The atoms of Democritus can well be thought of as tiny spheres of hard material; a bag of marbles or of shot might represent them. The elements of Plato and Aristotle cannot be symbolized in any such simple way. The figure on the opposite page shows what the Venetians of the sixteenth century thought of them.

Thus symbols for the atoms of Democritus can be realistic; they may indeed be models of these atoms; but symbols for the elements of Plato must be idealistic; and they are seen to be allegorical. Now, whatever may be said for the use of allegory in other realms, it is useless and misleading in the realm of physical science. And regarding

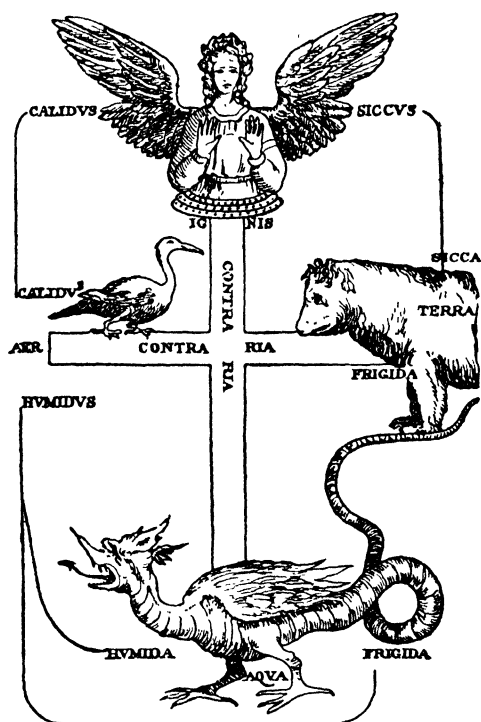
* From Plato's *Timæus*.

Aristotle; whilst by teaching the inductive method of investigation he appears to have laid the foundations of a true philosophy of science, yet by appropriating and extending the Platonic idea of the elements he must be held partly responsible for darkening the counsel of the professed seekers after scientific truth. To what extent allegory, aided in some measure by the religious sanctions of the Middle Ages, misled men during the centuries when the practice of alchemy was pursued with feverish zeal, will shortly appear; but it was Boyle, the "Sceptical Chemist" who brought men back to Nature undisguised, and taught the true idea of an element; and it was Dalton who built the modern atomic theory on an intellectual foundation which was truly laid by Democritus.

The influence of Greek philosophy on human thought was felt for more than a thousand years; and during all this time the minds of men as they contemplated Nature

were at the view-point of Aristotle rather than at that of Democritus. That is to say, metaphysics intruded into science; the properties of things, fancied or real, took the place of things themselves, and the progress of science was impeded. Thus the wildest allegory was used in place of plain language in the description of natural phenomena, and the symbolism of science became fantastic.

Now metaphysics has its place in human thought, but it should not distort the record of scientific facts. It is well for the scientific man to recognize that the phenomena he describes are conditioned



Alchemical Representation of the Transmutation of the Elements

Elements which are adjacent, and have properties in common, are transmutable; those which are "contraria", and have no such properties, are not.

not only by the external facts themselves, but also by the quality of the human mind; and even to confess that the external world itself, considered as a purely objective reality, can never be known in an absolute sense. Yet, unless he deliberately dismisses such considerations from his mind when engaged in scientific pursuits, and assumes that things are in themselves just what they appear to him to be, he will make no progress. This is an attitude towards Nature which the philosophers of the Middle Ages failed to take; they were not truly men of science, the modern scientific spirit had not yet been born.

Galen, in Rome (A.D. 130–201) based his system of medicine on the four elements of Aristotle. These four “elements” embraced all possible properties of things, and gradations between them; and the body of man was kept in health only when all its properties were rightly proportioned. Hence the function of medicine was to bring back to normal proportions the properties of the body whose relations had been disturbed by sickness; and the physician’s art was the discovery and administration of medicines to this end. It was not possible that scientific truth with regard to the body could be discovered when the mind of the physician was obsessed with such an idea as this.

It would appear that, later on, the Aristotelian elements were found to be too impalpable; so that whilst they remained as the ultimate expression of the nature of the Universe, elements which were more material were substituted for them in the workaday world of the alchemists. Thus, according to Geber, a notable alchemist of the eighth century, the proximate elements of matter were two: “mercury” and “sulphur”. Yet even these were not elements in the modern sense; for they still stood for principles or properties. Thus the term “mercury” represented ductility, fusibility, and lustre; while “sulphur” stood for combustibility. So “mercury” was not mercury, nor “sulphur” sulphur. It is plain that the Aristotelian or even the Platonic philosophy was showing itself again in such elements. Nevertheless there was something missing even here; these properties were not enough. Consequently a third element was added by Basil Valentine in the fifteenth century, viz. “salt”; not common salt by any means, but something that stood for permanence and unalterability by heat. Of these three elements, then, the metals were composed; and according to the proportion of the elements so were the properties of a metal.

These same elements were adopted by Paracelsus, the enemy of

alchemy and the founder of iatro- or medical chemistry. Iconoclast as he was, Paracelsus was nevertheless held in bondage by the old philosophy, for he connected together the whole of man and the elements, earlier and later, in the following scheme:

Soul	Spirit	Body
Mercury	Sulphur	Salt
Water	Air	Earth

Such a philosophy was hopelessly unscientific; it revealed a mind so perverted with age-long error as to fail to profit by experimental evidence.

Paracelsus, indeed, although making valuable additions to knowledge by the application of chemistry to the preparing of medicines, transferred the symbolism which the alchemists had employed for the metals to parts of the human body. Thus the sun was associated with the heart, the moon with the brain, Jupiter with the liver, Saturn with the spleen, Mercury with the lungs, Mars with the bile, and Venus with the kidneys; whilst the genius presiding over the functions of the stomach was a demon named Archæus, to whose operations the processes of digestion were due.

The philosophy of the alchemists was saturated with symbolism. At the foundation of this philosophy was the idea of the unity of matter, which was represented by a serpent or dragon devouring its own tail, and by the legend in Greek: "One is All". Prominent, too, among alchemistic symbols was the "sign of the crab", consisting of two concentric broken circles with a number of fine lines attached to them, which signified the transmutation of metals.

Some of the alchemistic symbols were of very ancient origin. They were borrowed from the Greeks, who in turn had derived them from the Egyptians. From astrologers of old the alchemists took symbols for the sun, moon, and five planets, and applied them to their seven metals. Thus the following signs frequently occur in alchemistic pictures:

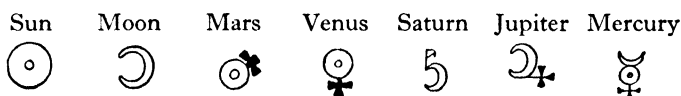
Gold	Silver	Iron	Copper	Lead	Tin	Mercury
						

It is easy to understand why the sun and moon were made to symbolize gold and silver respectively. Iron was readily associated with Mars, and the symbol represents the shield and spear of the war god; copper was linked with Venus and its sign was the mirror of the goddess, a sign, however, which can be traced from the Crux

ansata of the Egyptians  and the Assyrian symbol of Astarte .

dull lead was connected with Saturn, with a hook or scythe as symbol; and tin with Jupiter whose sceptre or throne is the sign of the metal; whilst the sign for mercury is the staff of Hermes surrounded with a serpent.

These symbols seem to be of Hindu origin since they can be compared with the following Hindu monograms of the sun, moon, and planets:



The alchemists of the sixteenth and seventeenth centuries interpreted these metallic symbols as expressing the properties of the metals in this way:

Gold.—The circle shows the perfection of the metal, and also its heaviness, because this figure covers the greatest quantity of matter with the least extension from the centre.

Silver.—The half-circle symbolizes silver as half gold.

Iron.—The symbol shows iron to be gold at the bottom, with the upper part volatile and "half corrosive". If this upper part were removed the iron would become gold.

Copper.—The body of copper is gold according to the symbol; but this is joined with a "corrosive" base.

Lead.—The symbol for lead is "the character for tin inverted, with the corrosive passing through the middle".

Tin.—An interpretation is not given, but the symbol seems to show tin to be silver with a corrosive base, as copper is gold with a corrosive base.

Mercury.—According to the symbol, mercury is silver at the top, gold in the middle, and corrosive at the bottom.

For "corrosive" read oxidizable, or able to be corroded.

The following interpretation of these ancient symbols is, however, given by Hassenfratz and Adet (1788):

Metals are divided into two classes: solar or coloured metals, and lunar or white metals; and these two classes are subdivided into perfect, semi-perfect, and imperfect metals. Perfection is symbolized by a circle , semi-perfection by a semicircle , imperfection by a cross or dart,  or . Thus the circle is

common to all metals of class I, e.g. gold ☉, copper ♀, iron ♂, antimony ⚛, in all of whose symbols, except that of gold, it is combined with a sign of imperfection.

Silver is the semiperfect lunar metal, having the sign ♄; tin ♄ and lead ♄ also have the semicircle combined with the cross; whilst mercury ☿ combines lunar and solar elements with the sign of imperfection. Hassenfratz and Adet add that this is a "whimsical regulation", which, however, "pleases the fancy of most people".

Operations also were symbolized. Thus the solution of a metal by an acid was represented by a wild beast devouring the metallic symbol. So a lion devouring the sun or moon means an acid dissolving gold or silver. A green lion, however, biting the sun, symbolizes mercury amalgamating with gold. Philosophic mercury was sometimes symbolized by a lion with wings, and philosophic sulphur by a lion without wings.

The accompanying picture bears the legend: "I am an old,



Alchemical representation of Solution of Gold in Aqua Regia

infirm, debilitated man. My soul and spirit leave me, and I assimilate the black crow." That this change is taking place can be seen from the centre of the picture. Above the circle are the symbols of the seven metals, whilst below it the elements are spending their strength to bring about the change. The interpretation of the picture seems to be that gold is being dissolved in *aqua regia*, thus losing its metallic nature (soul) and lustre (spirit), symbolized by flying birds, whilst it combines with the acid, which is represented by the black crow.

In ways like this the alchemists symbolized the substances and operations of their art in the age before modern science was born. Nevertheless there were among them men who desired to discover the properties and combinations of metals, without any ulterior philosophic purpose; and these, by their more unprejudiced labours, added greatly to human knowledge of the material world.

It will now be profitable, in pursuit of our theme, to observe how the later alchemists and their successors extended and elaborated the astrological symbols for the metals. And it is interesting first to notice that the following symbols are said to have been used by Basil Valentine, in the fifteenth century, to represent the four elements:



Fire



Air



Earth



Water

Fire and Air are light and rise; probably this is why the triangles which symbolize them point upwards. Earth and Water are heavy, and fall; this, we may suppose, is why they are symbolized by downward-pointing triangles. The waves in the sign for water are derived from the ancient Egyptians, and are also the zodiacal sign of Aquarius. Later, however, in the eighteenth century, the sign for water became ∇ . Antimony was $\odot$, the sign of copper inverted; sulphur was $\triangle$ because it combined the element of Fire with corrosiveness; and sulphide of antimony became $\odot$. Thus a compound symbol or formula was produced by combining two elemental formulæ. Again, Aqua Fortis was ∇ , and Aqua Regia ∇ ; Spirit was $\sim$, and to sublime was $\simeq$, a sign identical with the zodiacal sign for Libra, the Balances. Another

derived sign was  for mercurius sublimatus, whilst , showing the sign for precipitation as an inversion of that for sublimation, represented mercurius calcinatus. The following symbols, also, are suggestive: lead foil , copper foil , beaten gold .

Signs such as these show a distinct advance on the early alchemistic symbols; for there is some recognition of the composition of substances, and allegory has disappeared.

When the nature of chemical change began to be recognized, an attempt was made to represent chemical reactions in diagrammatic form, and to infer the direction of a reaction from numerical values of affinity based upon the ideas of Geoffroy and Bergmann.

Geoffroy, who was the first to give definite expression to ideas upon chemical affinity, had an elaborate set of symbols for reacting substances. He arranged these in tabular form to indicate different degrees of attraction between different substances. On the preceding page is Geoffroy's table of Affinities,* with the key for its interpretation.

In each vertical column the affinities of the different substances for the first substance diminish downwards, so that no substance could be expelled from combination with the first by any following it; but, conversely, a substance would be expelled from combination with the first by any preceding it.

Thus, consider the substances in the second column, the first member of which is hydrochloric acid (*acide du sel marin*). Tin is said to have the greatest affinity for this acid; and affinities are shown to diminish through regulus of antimony, copper, silver, and mercury to gold.

Or consider column eight, whose first member is "metallic substance". The affinities of acids for metallic substance are shown in the order: hydrochloric, sulphuric, nitrous (? nitric), acetic; which in the case of three out of four of these acids is the true order.

It is clear, therefore, from this table that Geoffroy had some knowledge of the reactivities of different classes of substances; e.g. the relative strengths of acids and bases, and the electropositiveness of metals.

A similar table of "Elective Attractions" was compiled by Berg-

* *Table des différents rapports observés en Chimie entre différentes Substances*, par M. Geoffroy l'aîné, *Mém. de l'Acad. des Sciences*, 1718, p. 202.

mann.* It is given here in abridged form, for sulphuric and hydrofluoric acids, modern formulæ being added to the names by way of explanation:

TABLE OF ELECTIVE ATTRACTIONS (BERGMANN)

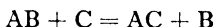
REACTIONS IN THE WET WAY

Sign.	Name.	Sign.	Name.
+ 	Vitriolic Acid (H_2SO_4)	+ 	Acid of Fluor (HF)
 p	Pure Ponderous Earth (BaO)	 p	Lime (pure calcareous) (CaO)
 √ p	Pure Vegetable Alkali (KOH)	 p	Pure Ponderous Earth (BaO)
 √ mp	Pure Mineral Alkali (NaOH)	 p	Pure Magnesia (MgO).
 p	Lime (pure calcareous) (CaO)	 √ p	Pure Vegetable Alkali (KOH)
 p	Pure Magnesia (MgO)	 √ mp	Pure Mineral Alkali (NaOH)
 p	Pure Volatile Alkali (NH_3)	 p	Pure Volatile Alkali (NH_3)
	Pure Clay (Al_2O_3)		Pure Clay (Al_2O_3)
 O	Calx of Iron (Fe_2O_3)	 O	Calx of Iron (Fe_2O_3)
 h	Calx of Lead (PbO)	 h	Calx of Lead (PbO)
 2	Calx of Tin (SnO_2)	 2	Calx of Tin (SnO_2)
 ♀	Calx of Copper (CuO)	 ♀	Calx of Copper (CuO)
 ♀	Calx of Mercury (HgO)	 ♀	Calx of Mercury (HgO)
)	Calx of Silver (Ag_2O)	)	Calx of Silver (Ag_2O)
 ○	Calx of Gold (Au_2O_3)	 ○	Calx of Gold (Au_2O_3)
 ○	Calx of Platina (PtO_2)	 ○	Calx of Platina (PtO_2)
	Water (H_2O)		Water (H_2O)
	Phlogiston		Pure Silicious Earth (SiO_2)

* *De attractiombus electionis* (Upsala, 1775).

There are several interesting things about this table. First, it must be understood that the substances following sulphuric acid in the first column, and hydrofluoric in the second, are placed in the order of what is supposed to be their decreasing affinity for these acids. This is plainly so with the metals, whose calces or oxides stand roughly in the order of their known electropotential values. The order of elective attractions is nearly the same in both lists, which accords with the fact that the relative affinities of different bases are independent of the acid with which they react. There are, however, notable exceptions. Thus baryta is represented as having the greatest elective attraction for sulphuric acid, and lime for hydrofluoric acid. This reveals the defect of the doctrine of affinity held by Bergmann; for this chemist regarded the formation of an insoluble compound as a sign that a powerful affinity existed between baryta and sulphuric acid. "Amongst the substances hitherto tried," said Bergmann, "vitriolic acid adheres most tenaciously to caustic terra ponderosa [$\text{Ba}(\text{OH})_2$], which when added to a solution of vitriolic tartar [K_2SO_4] generates the ponderous spar [BaSO_4] which remains insoluble at the bottom."

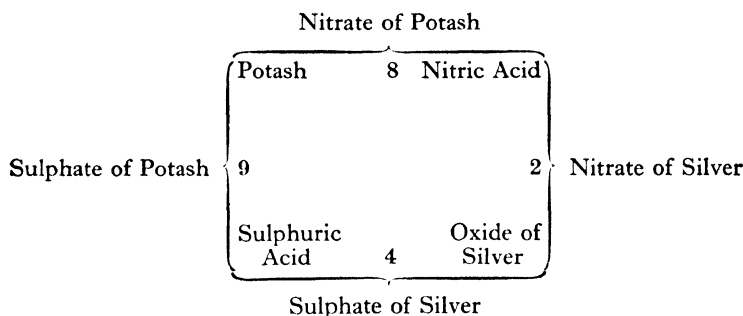
So Bergmann held that if the reaction:



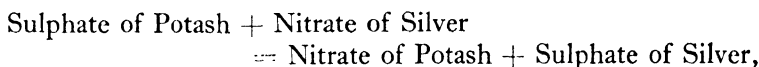
occurred, this proved that C had a greater affinity for A than B had. The conditions of the reaction, the solubilities of the substances concerned, and the possibility of reversing a chemical change, were not considered by Bergmann.

The symbols themselves present some new features. The symbol for water is the ancient one, and that for earth, with a little decoration, does duty for alumina. The symbols for the various alkalis resemble one another; the downward-pointing angle represents non-volatility, and the upward-pointing angle volatility. It is interesting to observe the symbol for phlogiston here. It must be remembered that at this date (1775) the phlogiston theory was nearing its end, and was soon to receive its *coup de grâce* at the hands of Lavoisier. Consequently the symbols in this table do not accord with pure phlogistonism. According to the phlogiston theory the calces of metals were elements, and the metals themselves compounds of their calces with phlogiston. Yet, according to Bergmann's system, the calx of a metal is a compound of the metal and "calx"; and there is no room for phlogiston; whilst, to avoid confusion between the calx of a metal and lime, lime is called pure calx, $\nmid\rho$.

Now consider the following representation of a chemical reaction which appears in a book published in Venice in 1792:



This may be expressed in a modern way as follows:

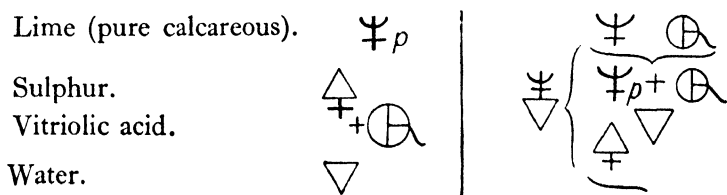


the direction of the reaction being left undetermined. This direction was supposed to depend upon the power of the predominating affinity, and could therefore be discovered by a simple calculation, thus:

Attractive force between potash and sulphuric acid	= 9	} sum = 11
" " " silver oxide and nitric acid	= 2	
" " " potash and nitric acid	= 8	} sum = 12
" " " silver oxide and sulphuric acid	= 4	

So because 12 is > 11 nitrate of potash and sulphate of silver would be formed from sulphate of potash and nitrate of silver.

Such an interpretation of chemical reactions appears naïve to-day. It corresponds with Bergmann's doctrine of affinity, which makes a chemical reaction depend only on affinity and ignores the influence of mass, i.e. the concentrations of the reacting substances within the sphere of action. Bergmann, however, represented such reactions symbolically, with a gain in picturesqueness. The following scheme represents the reaction between "calcareous hepar", i.e. calcium polysulphide, and "vitriolic", i.e. sulphuric acid:



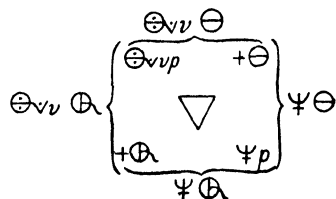
This is the interpretation of the figure. On the left is the sign for calcareous hepar, compounded of the signs for lime and hepar or sulphur; though the latter sign is inverted. In the centre of the figure beyond the vertical bracket, is the sign for water, the medium in which the reaction takes place. In the reaction lime and sulphur are shown separated, the lime thus being represented as pure (p), whilst into the water vitriolic acid ($+ \textcircled{\Delta}$) is brought [$+$ is the sign for acid]. At the top of the figure is the sign for vitriolate of lime; its two parts are shown separately, but the lime has lost its purity in combination, whilst the acid has lost its acidity. The downward-turned horizontal bracket signifies precipitation, i.e. it indicates that vitriolated lime, or calcium sulphate, separates as an insoluble solid. The half bracket, turned downward, below the sulphur, also signifies the precipitation of this substance. The lower right-hand corner of the figure is left incomplete. Was Bergmann conscious of the incompleteness of his explanation of the change? Probably not. The actual reaction which was thus represented is this:



The evolved hydrogen sulphide was overlooked; but it must be remembered that the chemists of Bergmann's day (1770–80) did not understand that an acid contained hydrogen, and therefore were not likely to recognize that a gaseous compound was a necessary product of the reaction.

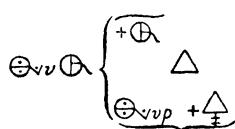
Other examples of Bergmann's formulæ may now be given; these are taken from *A Dissertation on Elective Attractions* published in English in 1785. Bergmann recognizes single elective attractions, such as might be represented thus: $\text{AB} + \text{C} = \text{AC} + \text{B}$; and double attractions, which may be symbolized by the equation: $\text{AB} + \text{CD} = \text{AC} + \text{BD}$. The example just given would be, according to Bergmann, a case of single attraction; for he believed that the change consisted simply in the replacement of sulphur combined with lime by sulphuric acid. Here, however, is a case of double attraction, i.e. what we should call double decomposition:

- | | |
|-------------------------|---------------------------------------|
| $\oplus \vee p$ | Pure fixed vegetable alkali (potash). |
| Ψp | Pure calcareous earth (lime). |
| $+\ominus$ | Marine acid (hydrochloric acid) |
| $+\textcircled{\Delta}$ | Vitriolic acid (sulphuric acid) |
| ∇ | Water |

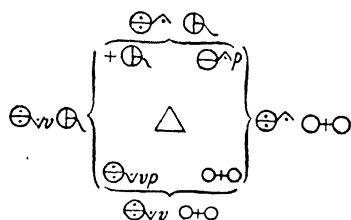


This is the interpretation: vitriolate of potash and muriate of lime are brought together in aqueous solution, and when they react muriate of potash remains in solution whilst vitriolate of lime is precipitated. We should represent the reaction thus: $\text{CaCl}_2 + \text{K}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{KCl}$. We have the advantage of simplicity; but Bergmann, besides picturesqueness, has the advantage of showing the medium in which the reaction is brought about.

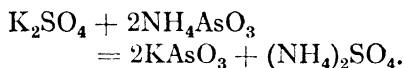
We have wet-way and dry-way reactions; so had Bergmann; and to represent the exchange of water for fire it was only necessary to invert the central triangle in the figure. Here are reactions of single and double attraction carried out in the dry-way by means of heat. The new signs in these reactions are: $+$ $\triangle$ phosphoric acid, $\odot\odot$ arsenic acid, $\ominus^\wedge$ volatile alkali (ammonia), $\triangle$ "matter of heat".



Reaction of Single Attraction.—Heat sulphate of potash with phosphoric acid and obtain phosphate of potash with volatilization of sulphuric acid: $\text{K}_2\text{SO}_4 + \text{P}_2\text{O}_5 = 2\text{KPO}_3 + \text{SO}_3$.



Reaction of Double Attraction.—Heat together sulphate of potash and arsenate of ammonia, and thus obtain arsenate of potash with volatilization of sulphate of ammonia:



Bergmann's work commanded the great respect of his contemporaries, and there is no doubt that it marked an advance on anything that preceded it.

Alchemistic symbols for the metals persisted until the end of the eighteenth century; for J. B. Richter, in a work published in 1798—*Ueber die neuern Gegenstände der Chemie*—employed such symbols in setting forth the quantitative relations between bases and acids which neutralized one another.

Among the signs used by Richter which have not yet been noticed

are these: manganese , antimony , uranium , nickel , cobalt , bismuth , zinc . Such signs seem to be quite

arbitrary; e.g. it would be difficult to say why the sign for bismuth is that for cobalt inverted.

The great experimenters of this period, however, appear to have had no use for symbols. Cavendish, Priestley, and Scheele described their experiments in language which, though often obscured by the phlogistic theory, was devoid of symbolism. Nevertheless the need for symbols was still felt by those who desired to systematize the science; and it is interesting to know that Lavoisier, the greatest systematizer of the period, employed symbols, some of which were inherited from the alchemists.

Thus, in 1782, Lavoisier used the following symbols:

 for iron, which is the ancient symbol; ∇ for water, also the ancient symbol;  for the newly discovered and newly named oxygen; and $\ominus \text{H}$ and $\triangle \text{H}$ for nitric acid and nitrous air (nitric oxide) respectively. The former of these two symbols seems unfortunate, since the sign $\ominus$ was earlier used for common salt; whilst $\oplus$ represented nitre. The cross in each symbol, however, stands for an acid in Bergmann's notation; and since $\triangle$ is the old symbol for air, the symbol $\triangle \text{H}$ appropriately represents an acid gas.

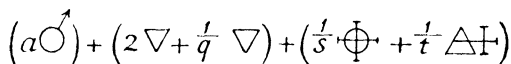
It would seem that the recognition of the indestructibility of matter must be essential to the adequate understanding of any chemical change; yet we do not find this principle understood until the time of Lavoisier. Lavoisier assumed it to underlie chemical change, and also proved its truth by direct experiment. Therefore he was properly the originator of the chemical equation, although necessarily this familiar thing could not take its present shape in his hands.

Lucretius, indeed, had affirmed that "nothing is created"; but Lavoisier said: "Nothing is created, either in the operations of art or in those of nature, and it may be considered as a general principle that in every operation there exists an equal quantity of matter before and after the operation; that the quality and quantity of the constituents is the same, and that what happens is only changes, modifications. It is on this principle that is founded all the art of performing chemical experiments; in all such must be assumed a true equality or equation between the constituents of

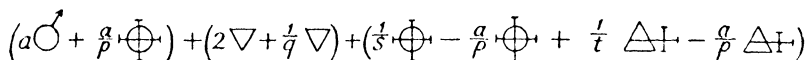
the substances examined, and those resulting from their analysis."

Here evidently we are at the birthplace of the chemical equation; yet we cannot find in the writings of Lavoisier this instrument as we know it; for our chemical equation depends as much on the atomic theory as on the doctrine of the conservation of mass. If we wish to see the cumbrous way in which an equation was written before the days of Dalton and Berzelius, when symbols did not stand for atoms, we have only to consider how Lavoisier represented such a chemical change as that between iron and nitric acid, remembering the meaning of the symbols already given.

This, then, is how the bringing together of iron and nitric acid in aqueous solution was symbolized by Lavoisier * in 1782:



This scheme represents a parts of iron reacting with 1 part of nitric acid, composed of $1/q$ part of water, $1/s$ part of oxygen, and $1/t$ part of nitrous air, in presence of 2 parts of water added to dilute the acid. The products of the reaction are shown by the following expression:



which represents the oxidation of the iron by the removal of a/p parts of oxygen from nitric acid, and the consequent escape of an equivalent quantity of nitrous air. This statement might be equated with the former one, except for the last formula, representing a/p parts of nitrous air missing, because it has escaped as gas. Thus it shows the matter which remains to be weighed on a balance in the open air, rather than the sum-total of the matter existing in its redistributed form. Evidently, however, Lavoisier recognized that a definite quantity of nitrous air was displaced by a certain quantity of iron, it being understood that if the gas that escaped could be collected and weighed the quantity of matter present after the reaction would be the same as before it.

Lavoisier was not content, however, with algebraic symbols for quantities which could be determined by experiment. By the use of the balance he ascertained what weight of oxide of iron remained

*Lavoisier's original expression is a little simplified to make it clearer.

after evaporation and ignition of the residue. The existence of a nitrate of iron escaped his notice; but the quantities of oxide of iron produced, and of water and acid remaining, were determined by him to be as follows:

$$(\cdot 2 \textcircled{\circ} + \cdot 058 \textcircled{\oplus}) + (2.5 \nabla) + (\cdot 192 \textcircled{\opl�} + \cdot 192 \triangleleft)$$

Such symbolic notation was greatly in advance of that of Bergmann; yet it has passed quite away because its author, in spite of his great intellectual power and equipment, and accurate quantitative methods, missed the atomic theory, with its simplified interpretation of chemical reactions.

In 1787 there was published in Paris, *Méthode de Nomenclature chimique*, by MM. de Morveau, Lavoisier, Berthollet, and de Fourcroy, and an English translation appeared in London in the following year. As a supplement to this treatise, and with the approval of its distinguished authors, there was added *A New System of Chymical Characters adapted to the Nomenclature* by MM. Hassenfratz and Adet.

Recognizing the confused state of chemical symbolism which then existed, these authors set themselves to the work of reformation, so as to produce a system of characters worthy to be used in conjunction with the new nomenclature. Their work was scientific and thorough, and is worth careful attention; although, for reasons which will appear, it could not be of permanent value.

In the introduction to their work these writers say: "In our reformation of the chymical characters we are far from having the same design with the ancient chymists. They endeavored by every means to screen their science with a mysterious veil from the eyes of the vulgar; we ought on the contrary to use our utmost endeavors to render our knowledge as communicative as possible."

Then follows a trenchant criticism of Bergmann's symbolism. Bergmann's fundamental characters, say these authors, were four: the triangle, the circle, the crown, and the cross. The inverted triangle, with a bar ∇ was used for earth, the circle for salts, the crown for metallic substances, and the cross for acids. The earth sign, therefore, ought to express with modifications all kinds of earth. It is used to represent silica and alumina; but lime, magnesia, and barytes are represented by the following signs: Ψ Ψ Ψ ; and the

cross which should be used for acids is found in the signs for lime, copper, tin, lead, sulphur, antimony, and mercury. Moreover, the circle, which had been reserved for salts, was used by Bergmann, as well as semicircles and crosses, in the signs for metals.

"It should seem from this," continue our authors, "that he wanted to express some supposed likeness between the metals and the saline substances. One would be tempted to think, on perusing his tables, that there was an analogy between lime and the oxyds; for when he wanted to represent a metal oxydified, he always joined to it the character of lime."

If Bergmann really wanted to do this he was wiser than the men of his generation, who did not guess the true nature of lime.

"These incoherencies and absurdities," conclude Hassenfratz and Adet, "we cannot suffer them longer to exist." Hence a general reformation, on the following lines.

There are two great classes of bodies: simple and compound. Therefore there should be two great classes of characters: characters for simple bodies and characters for compounds, formed by joining together those for simple bodies. Bodies were divided into six genera with corresponding signs.

<i>Genera.</i>	<i>Signs.</i>
I. Substances entering into the composition of the greater number of bodies.	Right line in four different positions: $ $ — $/$ $\backslash$; also zig-zagged, e.g. ξ .
II. Alkaline and terrestrial substances.	Triangle; $\triangle$ for alkalis, ∇ for earths. Initial of Latin name within the sign, thus: $\triangle_P$ potash, ∇_C lime.
III. Combustible substances.	Semicircle $\smile$ $\frown$ $($ $)$.
IV. Metallic substances.	Circle; with initial letter within it, e.g. $\textcircled{F}$. The sign $\odot$, however, is retained for gold.
V. Acidifiable substances.	Square; initial letter within, e.g. $\boxed{M}$.
VI. Compound substances whose component principles are yet unknown.	Lozenge; initial letter within, e.g. $\textcircled{E}$.

22 SYMBOLS AND FORMULÆ IN CHEMISTRY

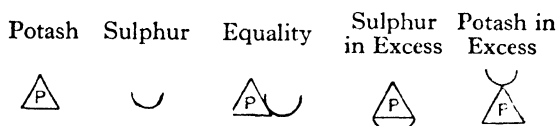
Here then are some of the signs of Hassenfratz and Adet:

I, II, and III.	IV.	V.	VI.
Σ Light.	(P) Platina.	[M] Muriatic acid.	(E) Ether.
Caloric.	(•) Gold.	[B] Boracic „	(A) Alcohol.
— Oxygen.	(A) Argentum.	[F] Fluoric „	(O) Fixed Oil.
/ Azot.	(H) Hydrargirum.	[A] Acetic „	(O _v) Volatile oil.
(P) Potash.	(S) Stannum	[T] Tartaric „	(B) Bitumen.
(S) Soda.	(C) Cuprum.	[O] Oxalic „	
(B) Barytes.	(P) Plumbum.	[C] Citric „	
(C) Lime.	(F) Ferrum.	[Bz] Benzoic „	
(M) Magnesia.	(Z) Zincum.	[Fm] Formic „	
(A) Alumina.	(M) Magnesium (Manganese).	[P] Prussic „	
(S) Silica.	(N) Nickel.		
) Hydrogen.	(B) Bismuth.		
(C) Carbon.	(St) Stibium.		
U Sulphur.	(K) Kobaltum.		
Phosphorus.	(As) Arsenicum.		
In reserve.	(M) Molybdenum.		
$\sim \sim \sim \sim$	(T) Tungstenum.		

Having symbols for the elements, let us see how these can be joined together to show compounds. Consider the characters ○ and □. These can be placed together in various ways; but three positions are clearly distinguishable, viz. ○□, ○
□, and □
○. Horizontal positions are taken to represent “reciprocal saturation”, which seems to mean, to borrow the language of the atomic theory still unthought of, that elements combine together atom with atom as

e.g. in CaO . Vertical positions indicate excess of the element represented by the lower character.

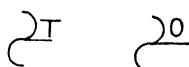
For example Potash was understood to form three different compounds with sulphur, and these were symbolized in the following way:



Again, azot combined with oxygen to form three different bodies which were symbolized thus:



These symbols will be understood when it is remembered that the lowering of the sign for oxygen shows the increase of the proportion of this element in the compound. Difficulties were experienced with the method, however, when compounds of greater complexity needed to be represented. Consider for example two organic acids. Tartaric acid was supposed to be composed of ten parts of carbon, five of hydrogen, and ten of oxygen; whilst oxalic acid consisted of nine parts of carbon, six of hydrogen, and ten of oxygen. Now in both of these compounds the carbon was in excess of the hydrogen, and, although the oxygen was in excess of both, its symbol was placed between the other two symbols. Nevertheless the method of symbolism was not refined enough to represent the numerical relations between the elements concerned, and so the symbol  might serve equally well or badly for both acids. Therefore Hassenfratz and Adet brought in initial letters to help them, and symbolized tartaric and oxalic acids respectively thus:



How simple it would have been to write the formulæ $\text{C}_{10}\text{H}_5\text{O}_{10}$ and $\text{C}_9\text{H}_6\text{O}_{10}$ respectively; but the atomic theory was not yet.

Among the signs will be observed that for Caloric |. This sign was used to show difference of state. It was thought unnecessary to employ it in representing the solid state, but for the liquid state

it was represented as present in a lesser amount, and for the state of gas or vapour in a greater amount. Thus for example we have lead $\textcircled{P}$, liquid lead $\textcircled{P}$, lead vapour $\textcircled{P}$.

It is interesting to notice that provision was made for the existence of numerous elements and compounds in all three states, although these states might be unknown. Thus a formula was provided for liquid and solid nitrogen and hydrogen as early as 1787. These are some of the formulæ for bodies in different states:

Body.	Solid.	Liquid.	Aeriform.
Azot ..	/	✓	/
Potash ..	$\triangle P$	$\textcircled{P}$	$\textcircled{P}$
Hydrogen ..	)	⤿	⤿
Carbon ..	C	⤿	⤿
Sulphur ..	⤿	⤿	⤿
Gold ..	$\textcircled{\cdot}$	$\textcircled{\cdot}$	$\textcircled{\cdot}$
Silver ..	$\textcircled{A}$	$\textcircled{A}$	$\textcircled{A}$
Iron ..	$\textcircled{F}$	$\textcircled{F}$	$\textcircled{F}$
Water ..	⤿	⤿	⤿

Lavoisier, Berthollet, and de Fourcroy commended the new formulæ thus: "We think the characters proposed by MM. Hassenfratz and Adet are far preferable to the ancient; that they have the advantage of painting to the sight, not words, but facts, and giving just ideas of the combinations which they represent."

We may agree with this judgment for there is no doubt that these signs mark the high-water mark of attainment in the symbolic representation of elements and compounds in the days before the atomic theory. It is true that for these symbols to be of use it would have been necessary for all previous symbols to be forgotten; for otherwise there would have been confusion. Thus it is rather confusing to find in this system the sign $\triangle$, formerly used for a gas, now employed for an alkali; and the sign ∇ , used in common by

the alchemists and Lavoisier for water, now employed for a fixed earth. It is interesting, however, to notice the initial letter of the alkali or earth within the symbol, e.g. $\triangle A$ for potash, and $\triangle A$ for alumina; and to observe that the symbols for metals are circles containing initial letters, e.g. $\odot N$ for nickel, and $\odot L$ for lead (plumbum), because there is here an anticipation of the symbols of Dalton, and, in the use of letters, of those of Berzelius.

All previous symbols have been forgotten; but the symbols of Hassenfratz and Adet have also been forgotten! Indeed it may almost be said of them that they were still-born, or at least that they died in infancy; they were too elaborately fashioned for common use, and were soon rendered quite superfluous. For, about sixteen years after these symbols had been devised, there occurred an event in chemistry which caused symbols to be used with a more definite and important meaning. That event was the enunciation of the modern atomic theory by John Dalton, of Manchester, in 1808.

Symbols, it seems, were first used by Dalton in 1803; and at the end of a paper read before the Manchester Literary and Philosophical Society, on 21st October of that year, occurs the following passage, accompanied by a table from which what follows is selected:

"An inquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new; I have lately been prosecuting this inquiry with remarkable success. The principle cannot be entered upon in this paper; but I shall just subjoin the results, as far as they appear to be ascertained by my experiments."

TABLE OF THE RELATIVE WEIGHTS OF THE ULTIMATE PARTICLES
OF GASEOUS AND OTHER BODIES

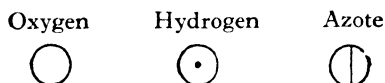
Hydrogen	..	..	..	..	..	1.0
Azote	..	..	..	..	..	4.2
Carbone	..	..	..	..	..	4.3
Ammonia	..	..	..	..	..	5.2
Oxygen	..	..	..	..	..	5.5
Water	..	..	..	..	..	6.5
Nitrous gas	..	..	..	..	..	9.3
Gaseous oxide of carbone	..	..	..	..	..	9.8
Nitrous oxide	..	..	..	..	..	13.7
Nitric acid	..	..	..	..	..	15.2
Carbonic acid	..	..	..	..	..	15.3
Carburetted hydrogen from stagnant water	..	..	..	..	..	6.3
Olefiant gas	..	..	..	..	..	5.3

Every symbol of Dalton was bounded by a circle, which no doubt suggested the boundary of the atom the symbol represented. The contents of the circle were sometimes arbitrary, though a plain circle stood for an atom of oxygen, and a black disc appropriately represented an atom of carbon. The symbols for non-metals and bases were arbitrary designs; but those for metals generally carried the necessary initial letters within them.

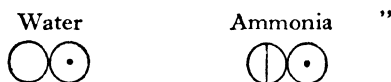
Dalton understood that compounds were formed by the union of the atoms of elements; therefore he placed the circular symbols for these atoms side by side to represent "atoms" of the compounds which were formed. Compounds might be "binary, ternary, quaternary", &c., according to the number of elementary atoms their compound atoms contained. He always assumed, however, that the smallest number of elementary atoms in a compound atom was the true number. So he supposed the compound atom of water to consist of one atom of hydrogen combined with one atom of oxygen.

Dalton's symbolic notation first saw the light in *A System of Chemistry*, by Thomas Thomson, M.D., F.R.S.E., published at Edinburgh in 1807. It was developed by Thomson in the following manner:

"If we represent an atom of oxygen, hydrogen, and azote, by the following symbols:

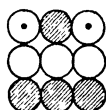


then an atom of water and of ammonia will be represented respectively by the following symbols:

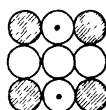


The following passage from Thomson is interesting, giving as it does a hint of what was afterwards known as isomerism: "A substance containing 9 atoms, such as acetic acid, must be of a very complex nature. And it is obvious enough that these 9 atoms might arrange themselves in a great variety of binary compounds, and the way in which these binary compounds unite may, and doubtless does, produce a considerable effect upon the nature of the compound formed. Thus if we make use of Mr. Dalton's symbols to represent the atoms of hydrogen, carbon, and oxygen, we may suppose the

9 atoms constituting acetic acid and succinic acid to be arranged thus:



or



Now undoubtedly these two arrangements would produce a great change in the nature of the compound."

In *A New System of Chemical Philosophy*, published at Manchester in 1808, Dalton presented his Atomic Theory with a plate of symbols (see p. 28) and the accompanying notes upon them.

This illustration contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

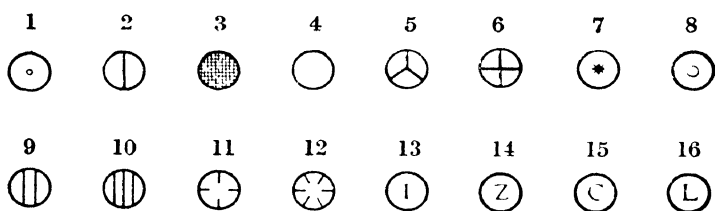
No.		No.	
1.	Hydrogen its relative weight 1	11.	Strontites 46
2.	Azote 5	12.	Barytes 68
3.	Carbone or charcoal .. 5	13.	Iron 38
4.	Oxygen 7	14.	Zinc 56
5.	Phosphorus 9	15.	Copper 56
6.	Sulphur 13	16.	Lead 95
7.	Magnesia 20	17.	Silver 100
8.	Lime 23	18.	Platina 100
9.	Soda 28	19.	Gold 140
10.	Potash 42	20.	Mercury 167

Then follow the names and compositions of a number of compound bodies:

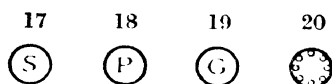
Fig.

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = ... 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen .. 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen .. 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen 6
25. An atom of carbonic oxide, composed of 1 of carbone and 1 of oxygen 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen 17
27. An atom of nitric acid, 1 azote + 2 oxygen 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen .. 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen .. 16
33. An atom of alcohol, 3 carbone + 1 hydrogen 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas 31
35. An atom of acetous acid, 2 carbone + 2 water 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid 35

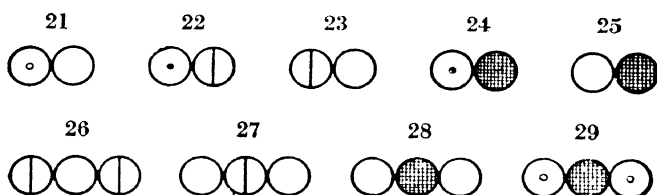
Single



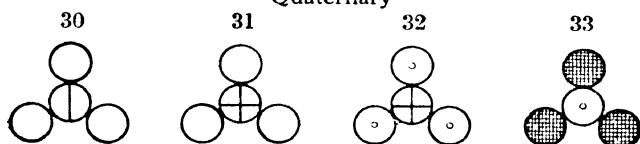
Binary



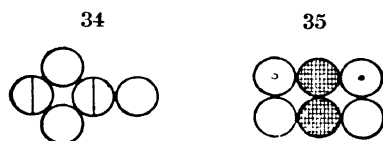
Ternary



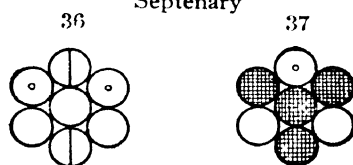
Quaternary



Quinquenary and Sextenary



Septenary



To inquire into the full significance of all these data would take us too far from our present purpose; but several important points may be noticed.

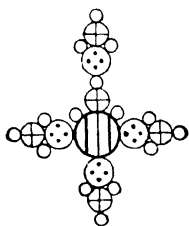
First, the so-called atomic weights were really equivalent weights. Dalton had no means of determining the real magnitudes of atomic weights.

Second, the term "atom" was applied alike to the ultimate particles of elements and of compounds.

Third, an acid, e.g. sulphuric acid, contained no hydrogen, nevertheless water was required to combine with ammonia and nitric acid to form a salt.

Fourth, soda and potash were symbolized as elements; nevertheless a little farther on Dalton recognized "Mr. Davy's very important discoveries" just made, that "they are metallic oxides". Sir Humphry Davy did not return the compliment; he did not accept the atomic theory, but used the word proportion instead of atom as involving no theoretical assumption.

The "arbitrary marks or signs" of Dalton did not prove acceptable to chemists. They were troublesome to reproduce, and therefore inconvenient; and they could never have survived the need to represent complex inorganic or organic compounds symbolically. The following formula, for example, represented alum:



To construct such formulæ was evidently an impossible task for chemists. Some of them, however, as well as some of the symbols of Hassenfratz and Adet, contained a hint for simplification. For it had already been found necessary in some cases to place the initial letter of the name of the element symbolized within the circle of its symbol; and so it might be asked why the circle should be retained since the bare initial letter might suffice.

The coming of modern symbols was an event of such importance that the circumstances which led up to it are worthy of detailed study. This study will be undertaken in the next chapter.

CHAPTER II

The Appearance and Development of Modern Symbols

The Electrochemical Theory and Symbols of Berzelius.—The electrochemical theory of Berzelius marks such an important stage in the development of theoretical chemistry that it will be well to give a detailed account of it. There are two reasons why this will be appropriate: first, the theory led directly to the modern system of chemical symbols, and the dualistic mode in which these were first employed; and second, the electrical theory of the atom developed by Berzelius should be carefully studied as the forerunner of the modern electronic doctrine of matter and of chemical affinity.

The work in which Berzelius set forth his views was entitled, *Théorie des Proportions chimiques, et Table synoptique des Poids atomiques*, and was published first in 1819, though this chemist had used his symbols as early as 1811.

After discussing a metaphysical theory of matter which assumed penetration of one particle by another in chemical combination, Berzelius adopted the atomic theory: “ Je choisirai la dénomination d’atome, parceque, mieux qu’aucune autre, elle exprime notre idée.” Atoms he represented as spheres; but “ compound atoms ” could not be spherical; and their size would depend upon the number of elementary atoms they contained; e.g. $(A + 2B)$ would occupy more space than $(A + B)$. Compound atoms could be of the first, second, or third, or more order. Sulphuric acid, potash, alumina, and water were “ des atomes composés du premier ordre ” because they contained only the “ radical ”, i.e. the other element and oxygen. Sulphate of potash and sulphate of alumina were compound atoms of the second order because they were composed each of two compounds of the first order; dry alum, being composed of sulphate of potash and sulphate of alumina was a compound of the third order; whilst crystallized alum “ containing many atoms of water combined with one atom of the double sulphate is an example of a compound

of the fourth order. One cannot say how many orders there may be."

As will appear later, here is the germ of dualism; though the reason for this manner of classification is not yet manifest. The following significant statement, however, follows: "With regard to the organic compound atoms, we are ignorant of the number of different orders in which they can combine, either among themselves or with inorganic compound atoms."

The electrochemical theory took shape in the mind of Berzelius in the following way.

Combustion was an exceedingly important phenomenon in chemistry; though its true significance had only lately been understood through the work of Lavoisier.

A new power had, however, been made available recently, viz. electricity. Electricity, moreover, was closely connected with fire, for by electric sparks combustible bodies were set on fire. It was also intimately connected with chemical action, for Volta's pile produced electricity by chemical means, and Davy's separation of the alkali metals by electrolysis was, reciprocally, the use of electricity to promote chemical separation. It is evident that Berzelius conceived the idea, though vaguely, of what we now call the transformation of energy; and, further, that he thought of electricity as the fundamental form of energy from which other forms such as heat and light were derived.

This is very interesting and significant, because of our modern view of electricity as the fundamental entity of the material universe.

Now there were two kinds of electricity—positive and negative; and it was these electricities which were the cause of the union of the atoms to form chemical compounds; chemical union was caused by electrical attraction between the atoms.

Every atom had upon it some of both kinds of electricity. Atoms, however, were not electrically neutral, but were charged either positively or negatively. How else should they attract each other? Thus it follows that the opposite charges on an atom are unequal; when the positive charge predominates the atom is electropositive, when the negative, electronegative.

So the elements were divided into two classes: electropositive elements, and electronegative elements. Elements of the first class, said Berzelius, as well as their oxides, always become electrified positively when in contact with elements or their oxides of the second class; oxides of the first class are basic, oxides of the second class are acidic. In other words, metals are electropositive, non-

metals electronegative. The electrical order of oxidizable elements accords generally with that of their oxides; and so the most oxidizable elements are those with the strongest affinities, as manifested by the elements themselves or by their oxides.

“By arranging the atoms in the order of their electrical affinities, one forms an electrochemical system, which, in my opinion,” said Berzelius, “is more suitable than any other arrangement to give an idea of chemistry.”

Oxygen is the most electronegative element; it is invariably and absolutely negative. All the others may be electronegative to one element and electropositive to another. For example, sulphur and arsenic are positive relatively to oxygen, but negative relatively to the metals. At the other end of the scale the metals of the alkalis and alkaline-earths are the most electropositive, and differ little amongst themselves; so that at the electropositive end there is no one element as electropositive as oxygen is electronegative. It has been supposed by many chemists that hydrogen is such a body; but this is not so, for hydrogen combines with potassium and is electronegative thereto. In the middle of the series are those elements whose electrochemical properties are little marked, and which might be classified in either category. These elements are not, however, devoid of electrochemical character; they are electropositive to those which precede and electronegative to those which follow them.

The following is the list of the elements in the order of their electro-potential according to Berzelius:

Electronegative

Oxygen.
Sulphur.
Nitrogen.
Fluorine.
Chlorine.
Bromine.
Iodine.
Selenium.
Phosphorus.
Arsenic.
Chromium.
Vanadium.
Molybdenum.
Tungsten.
Boron.
Carbon.
Antimony.
Tellurium.

Tantalum.
Titanium.
Silicon.
Hydrogen.
Gold.
Osmium.
Iridium.
Platinum.
Rhodium.
Palladium.
Mercury.
Silver.
Copper.
Uranium.
Bismuth.
Tin.
Lead.
Cadmium.

Cobalt.
Nickel.
Iron.
Zinc.
Manganese.
Cerium.
Thorium.
Aluminium.
Yttrium.
Glucinum.
Magnesium.
Calcium.
Strontium.
Barium.
Lithium.
Sodium.
Potassium.
Electropositive

"This," says Berzelius, "is thereabouts their order." There is no need to dilate upon the greatness of Berzelius in thus leading the world to a new view-point in chemistry. Broadly speaking, the order of electro-potential of the elements is that which would be accepted to-day. The non-metals head the list; hydrogen occupies an intermediate position, and is followed first by relatively inert metals, and then by metals which displace it with increasing ease, first from dilute acids and then from water. Certain alterations in detail have, however, been made. Fluorine is now regarded as the most electronegative element, and chlorine is more electronegative than sulphur or nitrogen. Then as regards the metals the following is the order of electro-potential of the principal metals recognized to-day:

Au, Pt, Pd, Ag, Hg, Cu, As, Bi, Sb, H, Pb, Sn, Ni, Co, Fe, Tl,
Cd, Zn, Mn, Al, Mg, Ca, Sr, Ba, Na, K, Rb, Cs.

It might be supposed, continues Berzelius, that this order would be the order of affinity of the elements for oxygen; but it is not, for this affinity depends much upon temperature. Thus at a certain temperature potassium reduces carbonic oxide gas, whilst at another temperature potassium oxide is reduced by carbon. Also temperature determines whether mercuric oxide is formed from or decomposed into its elements.

Next follows this great generalization: that oxides are divided into two classes, basic and acidic; also that a feebly acidic oxide behaves as a base to a stronger acidic oxide; and a feeble base plays the rôle of an acid to a more powerful base.

Berzelius then attempts to form a theory of electro-polarity, and expresses himself in the following way:

The preceding researches lead to this question: how is electricity present in an element? We have no precedent to guide us, and conjecture must be doubtful; nevertheless we try to show the cause of these phenomena.

We know that a body does not become electrified without showing two electricities, either in different parts of the same body, or at least in its sphere of activity. If in one body, then the two electricities are concentrated in two opposite points, and the electric state is similar to that of magnetic polarity. Further, if a body possesses polarity, this must be present in its smallest parts, i.e. in its atoms; upon this atomic polarity the electrochemical behaviour of an element depends, and the unequal intensities of the charges

are the cause of the affinities exercised. Bodies are electropositive or electronegative, according to the quality of the predominating charge ("Les corps sont donc électro-positifs ou électro-négatifs, suivant que l'un ou l'autre pôle y domine").

It may be pointed out here that the theory of Berzelius differs from the modern electronic theory of chemical union in this respect: according to Berzelius atoms attract and combine with one another because they are already charged; whereas according to the modern theory free atoms are neutral, but become charged by the transfer of electrons in the act of chemical union.

To continue with Berzelius: This uni-polarity—the property of being either electropositive or electronegative—does not explain all the phenomena. For there are two electronegative elements, oxygen and sulphur, which combine more intimately than do oxygen and copper, although copper is more electropositive than sulphur. The degree of affinity of bodies does not depend, then, only on their specific uni-polarity, but is derived principally from the intensity of their polarity in general. Certain bodies are susceptible of a more intense polarization than others, and must consequently have a stronger tendency to neutralize the electricity which is divided in their poles. That is why oxygen combines more intensely with sulphur than with lead (cf. SO_2 and PbO_2); for the positive pole of sulphur neutralizes a larger quantity of negative electricity in the dominant pole of oxygen than the positive pole of lead can neutralize.

This explanation is not satisfactory; it was an attempt by Berzelius to solve a problem long before the data for its solution became available. That there was any qualitative difference between the mode of union of oxygen with sulphur and with lead could not occur to Berzelius; but it is much to the credit of this great chemist that he realized the existence of a problem at all.

Berzelius further said that the electrochemical properties of an oxide depended almost entirely on the uni-polarity of the element oxidized. Thus an oxide would be electronegative with regard to other oxides when the elements oxidized were so related, and vice versa. For example, sulphuric acid is electronegative with regard to all metallic oxides because sulphur is electronegative with regard to all metals. The oxides of potassium and zinc, on the contrary, are electropositive with regard to the oxides of all elements towards which these metals are electropositive. This fact corrects an

inaccurate idea regarding oxygen in the anti-phlogistic theory. For we find that oxygen plays an indifferent part in oxides, since it enters equally into the composition of the strongest bases and the strongest acids.

Sometimes, however, it happens that an electropositive oxide acquires by higher oxidation properties less electropositive, so as to approach in properties the oxides of electronegative elements. Examples are stannic oxide and the higher oxides of manganese. In the case of the strongest bases, however, such as the oxides of sodium and potassium, the addition of oxygen produces a peroxide instead of an acid.

If these conjectures give a just idea of the connexion of elements with electricity, then what we call chemical affinity, with all its varieties, is only the effect of the electric polarity of atoms, and electricity is the fundamental cause of all chemical action, as well as the source of heat and light. It is thus the fundamental cause of all action in nature.

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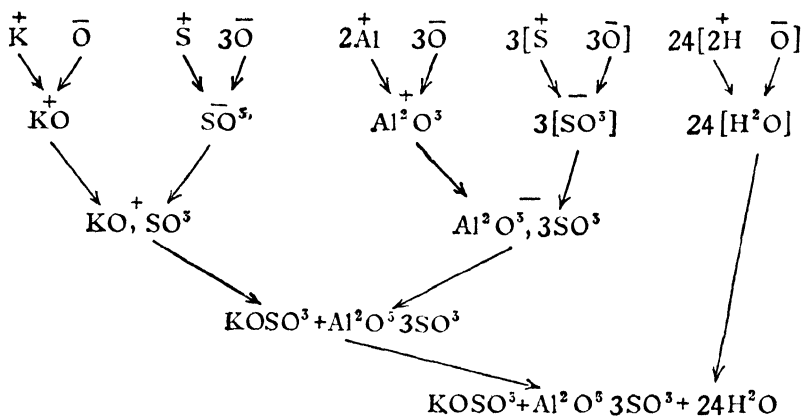
The above is a free translation of what Berzelius wrote in 1835. It is reproduced here, not only as a tribute to a great thinker in chemistry, but because it shows a true insight into the nature of inorganic compounds, and constitutes so remarkable a forecast of modern views.

It is necessary, however, to see what is the outcome of the theory of Berzelius. If these electrochemical views are correct, continues our author, it follows that every chemical combination depends essentially upon two opposite forces of positive and negative electricity; and that each compound must be composed of two parts united by reason of their electrochemical attraction, since there exists no other force to hold them together.

So every compound is divisible into two parts, of which one is positively and the other negatively electrified. For example, sulphate of soda is composed, not of sulphur, oxygen, and sodium, but of sulphuric acid and soda, both of which compounds can be divided again into two elements, one electropositive and the other electronegative. Similarly, alum cannot be considered as composed directly of its simple parts, but must be regarded as the product of the reaction of sulphate of alumina as the negative element with sulphate of potash as the positive element. Thus the electrochemical view is similar to that already explained regarding compounds of the first, second, and third order.

This is *dualism*, and it is seen to be the direct outcome of the electrochemical theory.

The following scheme shows the formation of alum according to the theory of Dualism.



We do not regard salts as composed in this manner to-day; and the reason why we do not will appear later. A serious objection to the dualistic hypothesis, moreover, an objection which led to its overthrow, was the fact that by its means it was not possible to account for the structure of organic compounds. This was not felt so seriously when organic chemistry was in its infancy; but with the growth of this branch of the science the development of other views became inevitable. "Every compound is composed of two parts," Berzelius had said; and this was the ground on which his theory was subsequently criticized. Nevertheless, he seems to have been aware that his views were not applicable to organic compounds; for in this connexion he wrote: "Les phénomènes électriques que nous venons de citer se manifestent principalement dans la nature inorganique: dans la nature organique, l'état des choses est différent."

As will appear, it is the great merit of the modern electronic view of the structure of chemical compounds to be able to account both for inorganic and organic compounds; both for electrolytes and non-electrolytes.

The use of formulæ above to show the composition of alum according to the dualistic theory anticipates a later phase of the work of Berzelius previously referred to, in which he develops the method of symbolism which, with some modification, we use at the

present day. To this important part of our subject we must now pay close attention.

Berzelius begins by showing how useful the symbol O for oxygen has been in setting forth the different stages of oxidation of an element. For example, the oxides of carbon have been thus represented: $R + O$, $2R + 3O$, $R + 2O$; the second formula representing the supposed composition of oxalic acid. "To make this usage general," says Berzelius, "it is sufficient to give each body a particular sign which represents the relative weight of its atom." Dalton, indeed, had done this; but Dalton's signs were different. For signs the initial letters of the Latin names of the elements were chosen by Berzelius. When the names of several elements had the same initial a second letter was added which was the first letter not common to both names. Thus C = carbon, Cl = chlorine, Cr = chromium, Cu = copper (cuprum), and Co = cobalt. A sign of a single letter was given preferably to a metalloid * and not to a metal. Thus B stood for boron rather than for barium. Nevertheless the symbols Cl, Br, Si, necessarily stood for chlorine, bromine, and silicon respectively, because the symbols C, B, and S had been otherwise appropriated.

"The number of atoms is indicated by figures. A figure to the left multiplies all the atoms placed to the right of it as far as the first + sign, or to the end of the formula. A little figure placed to the right of the letter and above it, like an algebraic exponent, multiplies only the atomic weight placed to its left. E.g. S^2O^5 signifies an atom of hypo-sulphuric acid, and $2S^2O^5$ signifies two atoms of the same acid."

Thus far the method of Berzelius is such as remains to the present day, except that it is usual to place the little figures below the line; thus S_2O_5 instead of S^2O^5 . The latter method of formulation is, however, still employed by French writers.

In what follows, however, Berzelius made what we are bound to regard as an unfortunate mistake.

"In all cases where two atoms of an element are combined with 1, 3, or 5 atoms of oxygen, as, for example, sulphur here, the clearness of the formula is much increased when a special sign is employed for the double atom. The most natural sign would be to double the initials so that they remain bound together to form one sign instead of two. But I have found that these formulæ are denoted most easily, and with equal clearness, by drawing a straight line

* The term metalloid was at this time used as synonymous with non-metal.

through the initial to represent two atoms. This line is placed in the lower third of the letter: thus P signifies one atom and P a double atom of phosphorus; As one atom and As a double atom of arsenic."

It is difficult for anyone unacquainted with the history of chemistry to understand the meaning of this. Why, for example, should the formula SO^5 be preferred to the formula S^2O^5 ; and why should there be any desire to represent double atoms of phosphorus and arsenic, since such combinations are not characteristic of these elements? The only answer that can be given to this question is that Berzelius thought double atoms, or, otherwise, diatomic molecules played a far more important part in chemistry than we now know them to play. Berzelius was much impressed with the law of volumes of Gay-Lussac, and the demonstration that what we now call the molecules of the simple gases consisted of double atoms; and it seemed to him that there was something sacrosanct about the double atom. He did not know what a small part the double atom really plays in the economy of the elements; how few of the elements in the state of vapour consist of double atoms. Thus a molecule was identified with two volumes so that one volume might be reserved for one atom; and thence was derived the volume-atom hypothesis, an idea which did much mischief to theoretical chemistry.

This explains but does not justify the barred formulæ. Why was Berzelius not content with his symbols for atoms and his figures to multiply the atoms? We can only regret the false step which this great man took.

Now let us see how Berzelius developed his formulæ.

"Compounds of the first order are designated as follows: $\text{CuO} + \text{SO}^3$ expresses cupric sulphate, and $\text{FeO}^3 + 3\text{SO}^3$ ferric sulphate. But when one wishes to express the composition of a double salt, that is, of a compound atom of the second order, the formula becomes in this way long and obscure; and since these atoms of the second order are generally either oxysalts or sulphosalts, it is easy to indicate the number of atoms of oxygen by points placed above the atomic symbols; and the number of atoms of sulphur can similarly be represented by commas if this is thought an advantage. Thus cupric sulphate becomes $\text{Cu}\ddot{\text{S}}$, ferric sulphate $\text{Fe}\ddot{\text{S}}^3$, alum $\text{K}\ddot{\text{S}} + \text{Al}\ddot{\text{S}}^3 + 24\text{H}$. In the same manner K signifies potassium sulphide, and KM potassium sulphomolybdate."

The idea was carried further by using the sign — for selenium

and + for tellurium as exemplified by the following formulæ:

$\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{K}}}\overset{\cdot\cdot}{\text{Mo}}$ Potassium oxymolybdate.

$\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{K}}}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Mo}}}$ Potassium sulphomolybdate.

$\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{K}}}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Mo}}}$ Potassium selenimolybdate.

$\overset{+}{\underset{+++}{\text{K}}}\overset{+}{\underset{+++}{\text{Mo}}}$ Potassium tellurimolybdate.

There is no doubt that all this was a retrograde step. Arbitrary symbols were a thing of the past. It had been the special mission of Berzelius to do away with them; yet here he is bringing them back again.

These abbreviated formulæ were used for a time, especially by mineralogists. Chemists, moreover, have no objection to writing the full formula for alum: they have far more complicated formulæ than that to write.

Here are the symbols for the elements introduced by Berzelius. Where the symbol differs from that in use at the present day the name of the element is added after it.

O, H, N, S, P, Cl, Br, I, F, C, Ta, Ti, Os, Au, Ir, R (rhodium), Pt, Pd, Hg, Ag, Cu, U, Bi, Sn, Pb, Cd, Zn, B, Si, Se, As, Cr, Mo, W, Sb, Te, Co, Ni, Fe, M (manganese), Ce, Al, Zr, Th, Y, G (glucinum), Mg, Ca, Sr, Ba, L (lithium), Na, K.

“ Ordinarily I commence a formula with the electro-positive element,” says Berzelius, “ and terminate it with the electro-negative element.”

“ These initials are derived from the Latin nomenclature which is common to naturalists of all countries; and are serviceable for all, without necessitating any change of language. No one will dispute that Latin presents in this respect a great advantage, as the majority of savants who have adopted these formulæ agree. If a French author, for patriotic reasons, changes the initials into those of the French language, and English, German, and Italian authors imitate his example, these formulæ will lose much of their clearness and precision without any other advantage. But we hope the enlightened spirit of the majority of true naturalists will not sacrifice real advantage to a puerile vanity. ‘ Science,’ as has well been said by Sir Humphry Davy, ‘ like that nature to which it belongs, is neither limited by time nor space, it belongs to the world, and is of no country and of no age.’ ”

Subsequent history has shown that mankind was equal to the

measure of broadmindedness here asked for. Nevertheless the French speak of azote for nitrogen, and use the symbol Az.

Sundry objections were raised to the new symbols, and these were met by the author. It was said that the symbols were wanting in clearness, led to error, and offered no advantage. To this Berzelius replied that the symbols could only be obscure to those who were unfamiliar with their interpretation, that nothing could be easier than to understand them; and that any error lurking within them was in the facts and not in their interpretation. It was further objected that the index figures used in the formulæ had a significance different from their algebraic significance, and therefore that the formulæ themselves were offensive to mathematicians. To this Berzelius replied in these words: "une semblable objection ne mérite pas d'être réfutée."

The symbols may of course be objected to on theoretical grounds. The purist may say that a letter is a symbol for a sound and therefore cannot be used properly as a symbol for a certain kind of matter. The symbols it may be said are arbitrary; but they are not more arbitrary than the names of the elements from which they are derived. It is no fault of the symbol Co that the word cobalt means a goblin; and the symbol Ni need not be regarded as evil because the name nickel means a demon.

This, however, is what Dalton, as late as 1837, thought of the symbols of Berzelius: "Berzelius's symbols are horrifying; a young student in chemistry might as well learn Hebrew as make himself acquainted with them. They appear like a chaos of atoms . . . and to equally perplex the adepts of Science, to discourage the learner, as well as to cloud the beauty of the Atomic Theory."

By this time, however, the chemical world had accepted the notation of Berzelius; and Dalton was left alone with his symbols. Thus the new symbols came to be used as a convenient shorthand for the elements, but more precisely as signs for their atoms.

This account of the work of Berzelius may be fittingly concluded by giving a selection of data from his *Table synoptique des Poids atomiques* (see Table, p. 41). To decipher the significance of the formulæ is an interesting and profitable exercise.

A few comments may be made upon these data. It must be remembered that, according to dualism, whilst basic oxides are bases, acidic oxides are also acids. Thus As_2O_5 is arsenic acid, and that is what the first formula, with its barred arsenic symbol, stands for. Similarly CO_2 is carbonic acid. According to the fourth column in

TABLE SYNOPTIQUE DES POIDS ATOMIQUES

Noms des Substances.	Formules.	Poids de l'Atome.		Contient pour Cent.		
		O=100.	H=1	Base.	Acide.	H
Acide arsénique ..	$\ddot{\text{As}}$	1440.08	115.39	65.28	34.72	
	$\ddot{\text{As}}^2$	2880.17	230.79			
	$\ddot{\text{As}}^3$	4320.25	346.18			
Acide carbonique ..	C	276.44	22.15	27.65	72.35	
Acide hydrochlorique	HCl	227.57	18.23	H=2.74	Cl=97.26	
Acide sulphurique ..	S	501.16	40.16	40.14	59.86	
Ammoniac ..	NH ⁺	214.47	17.19			
Ammonium ..	NH ⁺	113.48	9.09	N=78.00	H=22.00	
Arseniate sodique crist.	Na ⁺ As + 24H	4921.39	394.36	15.89	29.26	54.85
Carbonate calcique ..	CaC	632.46	50.68	56.29	43.71	
Chlorate potassique ..	KCl	1532.57	122.81	38.49	61.51	
Chloride phosphoreux	PCl	1720.24	137.84	22.80	77.20	
Chlorure mercurieux	HgCl	2974.30	238.33	85.12	14.88	
Chlorure mercurique	HgCl	1708.47	136.90	74.09	25.91	
Chlorure potassique	KCl	932.57	74.73	52.53	47.47	
Eau	H	112.48	9.01	11.09	88.91	
	2H	224.96	18.03			
Hydrate potassique	KH	702.40	56.28	83.99	16.01	
Hyposulphite sodique	NaS	993.23	79.59	39.36	60.64	
Magnésie	Mg	258.35	20.70	61.29	38.71	
Nitrate potassique ..	KN	1266.95	101.53	46.56	53.44	
Oxalate calcique ..	CaC	808.89	64.82	44.01	55.99	
Oxide baritique ..	Ba	956.88	76.68	89.55	10.45	
Suroxide de Barium	Ba	1056.88	84.69	81.08	18.92	
Sulfate calcique	CaS	857.18	68.69	41.53	58.47	
crist.	CaS + 2H	1082.14	86.71	32.90	46.31	20.79
Sulfate cuivrique						
crist.	CuS + 5H	1559.26	124.94	31.79	32.14	36.07

this scheme an acid itself is divisible into a basic and an acidic part. What is to be done with HCl then? It can only be divided into H and Cl, which can quite properly be called base and acid. This, however, is an acid containing hydrogen but not oxygen: a hydracid. Thus a hint was given here that hydrogen and not oxygen is an essential constituent of an acid. This important fact was not, however, realized by Berzelius.

Ammonium, it appears, is divided similarly by Berzelius into basic and acidic parts, but without justification.

The formula for arsenate of soda represents $2[\text{Na}_2\text{HAsO}_4, 12\text{H}_2\text{O}]$,

but the existence of a molecule of water within the arsenate itself, which is lost when the salt is converted into pyroarsenate by ignition, is not recognized. It is singular that the use of the term "chloride" is confined to non-metallic or metalloidal chlorides. Hydrate of potash is KO , H_2O , and is composed of the base KO and the acid H_2O ; whilst oxalate of lime is CaO , C_2O_3 , and sulphate of copper CuO , $\text{SO}_3 + 5\text{H}_2\text{O}$.

There are 353 pages of these formulæ in Berzelius's book; and they represent an amazing amount of accurate work; for they contain the quantitative results of numerous atomic weight determinations carried out by this indefatigable chemist. "After work extending over ten years," said Berzelius, "I was able, in 1818, to publish a table which contained the atomic weights, as calculated from my experiments, of about two thousand simple and compound substances."

It is noteworthy that atomic weights are calculated according to two standards; that of $\text{O} = 100$ and that of H (i.e. H_2) = 1. To Berzelius oxygen was the pole of chemistry, since it combined with nearly every other element; therefore it was natural to choose its atomic weight as the standard. It is easy, also, to understand the view that hydrogen, the lightest known element should be given the value 1 and taken as the standard. That $\text{H} = 1$, however, is only another example of the powerful influence of the double-atom idea.

To show how accurate was the work of Berzelius,* a few of the atomic weights calculated to $\text{O} = 16$ from the data given on p. 41 are here shown side by side with modern values:

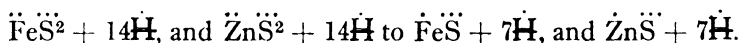
Element.	Atomic Weight.	
	Berzelius (1835).	Modern.
Arsenic	75.2	74.96
Carbon	12.23	12.00
Chlorine	35.42	35.46
Hydrogen	0.995	1.008
Nitrogen	14.17	14.008
Potassium	78.37	39.10
Sulphur	32.18	32.06

It will be noticed that the atomic weight of potassium has double

* "Most of these numbers," said Wurtz, "only differ in the decimals from those which we now adopt as true. Such is the result of the enormous amount of labour expended by the Swedish chemist upon the determination of the atomic weights. It is a lasting monument which he has raised to science and his own glory."

the present value. This accords with the formula KO for the oxide; for Berzelius did not realize that a metallic oxide might be of the type M_2O . Indeed at first, i.e. about the year 1814, he thought that metallic oxides must conform to the type MO_2 , as for example: NaO_2 , KO_2 , CaO_2 , FeO_2 , ZnO_2 , CuO_2 , PbO_2 ; consequently his atomic weights for the metals in these oxides were double, or, in the case of the alkalis, quadruple, their present-day values.

It was the work of his pupil Mitscherlich, published in 1819, which caused Berzelius to change a number of his atomic weights and formulæ. Previously the oxides of chromium and iron had been CrO_6 , CrO_3 and FeO_3 , FeO_2 ; but the isomorphism of chromates with sulphates necessitated the change of the chromium oxides to CrO_3 and Cr_2O_3 ; and the isomorphism of ferric and chromic alum required the oxides of iron to be Fe_2O_3 and FeO ; but the resemblance between the salts of ferrous iron and those of calcium, magnesium, zinc, &c., required the corresponding oxides to be of the type MO , with the consequent halving of the atomic weights. So the formulæ for ferrous and zinc sulphates were changed from:



Berzelius, however, did not take the further step of halving the atomic weights of the alkali metals and representing their oxides according to the type M_2O . That step was taken by Gerhardt, who represented these oxides as conforming to the water type.

It is not necessary to trace here the fortunes of atomic weights, and the changes they underwent at the hands of Dumas, Gerhardt, Laurent, and Cannizzaro, until, under the latter chemist they assumed values which were found to be in accord with the hypothesis of Avogadro, the laws of isomorphism and specific heats, and afterwards the periodic law.*

In *Chemical and Physical Researches*, by Thomas Graham, published in 1876, there are collected together various papers on the constitution of salts, and these contain interesting examples of Berzelian formulæ, some of which may be appropriately reproduced here:

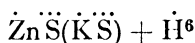
Thus it appears that in papers published during the period 1835-38 Graham employed dots for oxygen atoms, but that in 1841, and afterwards, he used the symbol O, so that his formulæ appeared in the orthodox dualistic guise.

* The classical account of this subject is given by Wurtz in *The Atomic Theory*, a volume in the "International Scientific Series".

Graham's views upon sulphuric acid and the sulphates are enlightening. Thus he regarded what we now formulate H_2SO_4 as a combination of sulphuric acid (SO_3) with water (HO). Indeed it was sulphate of water, being formulated $\text{H}\ddot{\text{S}}\ddot{\text{H}}$. The compound $\text{H}\ddot{\text{S}}\ddot{\text{H}}\ddot{\text{H}}$ ($= \text{H}_2\text{SO}_4, \text{H}_2\text{O}$) was regarded as a "primary sulphate", and a relation was shown between this sulphate and hydrated zinc sulphate, thus:



Sulphate of potash could then take the place of an atom of water, and with six more atoms the well-known zinc potassium sulphate resulted, and was formulated thus:



The following are interesting examples of Graham's formulæ:

Gypsum	$\text{Ca}\ddot{\text{S}}\ddot{\text{H}} + \text{H}$
Gypsum dried at 212°	$\text{Ca}\ddot{\text{S}}\ddot{\text{H}}$
Anhydrous gypsum (dried at 270°)	$\text{Ca}\ddot{\text{S}} -$
Anhydrite	$\text{Ca}\ddot{\text{S}}$

The difference between anhydrous gypsum and anhydrite is that the former can be rehydrated, but the latter is permanent. Anhydrous gypsum was therefore regarded as an *imperfect* body from which something was lacking, represented by the minus sign.

Hydrated oxalic acid was oxalate of water and had the formula $\text{H}\ddot{\text{C}}\ddot{\text{C}}\text{H}^2$, which, expanded, is $\text{HO}, \text{CO}, \text{CO}_2 + 2\text{H}_2\text{O}$; and if H_2O is written for HO , the formula is seen to be equivalent to ours.

The following names and formulæ of phosphates serve further to illustrate Graham's way of expressing chemical compounds, as well as to show the work of this great chemist on phosphoric acid:

First Class

Monobasic phosphate of water (meta-phosphate of water)	$\text{H}\ddot{\text{P}}$
Monobasic phosphate of soda (meta-phosphate of soda)	$\text{Na}\ddot{\text{P}}$

Second Class

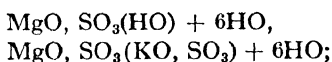
Bibasic phosphate of water (pyrophosphate of water)	$\dot{\text{H}}^2\ddot{\text{P}}$
Bibasic phosphate of soda and water (bipyrophosphate of soda) ..	$\dot{\text{Na}}\dot{\text{H}}\ddot{\text{P}}$
Bibasic phosphate of soda (pyrophosphate of soda)	$\dot{\text{Na}}^2\ddot{\text{P}} + 10\dot{\text{H}}$

Third Class

Tribasic phosphate of water (common phosphate of water)	$\dot{\text{H}}^3\ddot{\text{P}}$
Tribasic phosphate of water and soda (biphosphate of soda)	$\dot{\text{Na}}\dot{\text{H}}^2\ddot{\text{P}} + 2\dot{\text{H}}$
Tribasic phosphate of soda and water (phosphate of soda)	$\dot{\text{Na}}^2\dot{\text{H}}\ddot{\text{P}} + 24\dot{\text{H}}$
Tribasic phosphate of soda (subphosphate of soda)	$\dot{\text{Na}}^3\ddot{\text{P}} + 24\dot{\text{H}}$
Tribasic phosphate of soda, ammonia, and water (microcosmic salt) ..	$\dot{\text{Na}}\dot{\text{N}}\dot{\text{H}}^4\ddot{\text{P}} + 8\dot{\text{H}}$
Tribasic phosphate of magnesia and water (phosphate of magnesia) ..	$\dot{\text{Mg}}^2\dot{\text{H}}\ddot{\text{P}} + 2\dot{\text{H}} + 12\dot{\text{H}}$
Tribasic phosphate of magnesia and ammonia (ammoniacomagnesian phosphate)	$\dot{\text{Mg}}^2\dot{\text{N}}\dot{\text{H}}^4\ddot{\text{P}} + 2\dot{\text{H}} + 10\dot{\text{H}}$

Phosphate of water: how strange it sounds! Yet it is consistent dualism: for if NaO , PO_5 is phosphate of soda, then why should not HO , PO_5 be phosphate of water; indeed, what else can it be? Of course, our answer to this question is: first, that water is not truly basic, like soda, though if we give this answer we must not speak of acids as hydrogen salts; and second, that water here is an essential part of the acid, because without its hydrogen there would be no acid. Nevertheless, we shall agree that dualism is worthy of great respect.

In a paper published in the *Phil. Mag.* in 1842, Graham writes thus: "Crystallised sulphate of magnesia, and the double sulphate of magnesia and potash, I have represented thus:



considering the latter salt to be derived from the former, by the

substitution of sulphate of potash for that single atom of water, which is found to be much more strongly attached to the sulphate of magnesia than the other six."

Just as sulphate of potash can replace water in heptahydrated sulphate of magnesia, so it is able to convert monohydrated sulphuric acid into bisulphate of potash, thus:

Sulphuric acid of specific gravity, 1.78	..	HO, SO ₃ (HO).
Bisulphate of potash		HO, SO ₃ (KO, SO ₃).

Henceforth Graham adopts these more usual dualistic formulæ even to writing the small numerals below instead of above the symbols.

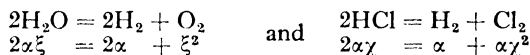
At this stage we may notice some more modern criticisms of Berzelius's symbols and of the atomic theory to which they gave expression.

The Calculus of Chemical Operations.—Sir B. C. Brodie, in a paper on "The Calculus of Chemical Operations",* criticized the symbols of Berzelius in a twofold manner. First, he objected to the symbols being placed in apposition, when addition and not multiplication of the units symbolized was meant. Thus he recognized that when Berzelius wrote the formula H_2O he meant $H + H + O$; but he approved of Sir John Herschel's objection to the ordinary formula, and his suggestion that it should be written $2H + O$. This objection, however, has now been waived for many years, if indeed it ever seriously existed; and it is only the veriest tyro in chemistry who thinks of multiplying atomic weights together. Brodie's second and more serious objection was to the use of atomic symbols at all, not only because they introduced the "atomic hypothesis" into every description of a chemical phenomenon, but also because they omitted to take account of the operation of chemical change itself.

Symbols, said Brodie, are of two kinds: symbols of things and symbols of operations on things. For instance, the word "dog" is a symbol for a domestic animal, the word "beating" is a symbol for an operation we can perform on the animal. And Brodie desired to have, and therefore invented, symbols for chemical operations which were independent of the "hypothesis of Dalton". Yet the operations were not independent of the matter acted upon; and so he claimed that the symbols, when once worked out, represented elements and compounds themselves, besides operations involved in their production.

The symbols α , ξ , and χ in the following equations were called by Brodie prime factors; α stood for the unit of hydrogen, and was called the modulus of the symbolic system; ξ and χ were symbols used to express the operations employed in the preparation of oxygen and chlorine respectively; but, as will be seen, they were not symbols for the elements themselves.

Here are equations for two simple reactions, according to the method of Berzelius, and that of Brodie:



Brodie claimed that his equations epitomized operations; that his symbols were symbols, not of quantities, but of operations. "We cannot," he said, "adopt the atomic symbol, and at the same time declare ourselves free from atomic doctrines. The symbols which are here employed impose no such limitation upon our view. They are simply symbols of operations."

It may reasonably be concluded from this that if oxygen and chlorine are produced by other means, other symbols will set forth their production. That is the case; and yet these symbols seem to be regarded as of general utility: "It will be found by trial that the symbol of oxygen . . . will satisfy all known conditions." Hence the following symbols, among others, for elements and compounds are given by Brodie in his lecture on "Ideal Chemistry".*

SYMBOLS OF THE UNITS OF CHEMICAL SUBSTANCES

Hydrogen	..	..	α	Nitrogen	..	..	$\alpha\nu^2$.
Oxygen	..	..	ξ^2	Carbon	..	..	κ .
Water	..	..	$\alpha\xi^2$	Acetylene	..	..	$\alpha\kappa^2$.
Sulphur	..	..	θ^2 .	Marsh Gas	..	..	$\alpha^2\kappa$.
Hydrogen Sulphide	..	..	$\alpha\theta$.	Olefiant Gas	..	..	$\alpha^2\kappa^2$.
Sulphuric Acid	..	..	$\alpha\theta\xi^4$.	Carbon Monoxide	..	..	$\kappa\xi$.
Chlorine	..	..	$\alpha\chi^2$	Carbon Dioxide	..	..	$\kappa\xi^2$.
Hydrogen Chloride	..	..	$\alpha\chi$.	Carbon Tetrachloride	..	..	$\alpha^2\chi^4\kappa$.
Iodine	..	..	$\alpha\omega^2$.	Chloroform	..	..	$\alpha^2\chi^3\kappa$.
Bromine	..	..	$\alpha\beta^2$.				

For the mathematical justification of these symbols the original paper in the *Journal of the Chemical Society* must be consulted. They are to be regarded, says the author, "as chemical equations turned into another form, and divested of a certain amount of superfluous and useless matter".

If these symbols are to be regarded simply as setting forth the mode of preparation of the elements and compounds they represent, with no relation to composition, they may be justified. Nevertheless chemists have universally agreed that their formulæ shall show the composition of substances without reference to manner of preparation; and they have, therefore, no use for Brodie's symbols. A scheme, indeed, which, e.g. represents hydrogen, hydrogen chloride, and chlorine by the symbols a , $a\chi$, $a\chi^2$, respectively, appears misleading until the effort of thought necessary to relate the symbols to the author's scheme has been made.

Yet the desire to develop a symbolic notation directly related to experimental facts was laudable; and it must be recognized that Dalton's atomic theory, now so familiar, and so completely justified, was at its inception speculative and indeed revolutionary; and one can understand the wish of a philosophic chemist not to commit himself to this theory whenever he wished to symbolize chemical facts.

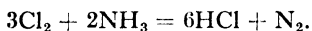
It is pertinent to inquire, however, if any symbols or formulæ are adequate to represent the facts. Consider this example given by Brodie:

3000 c.c. chlorine + 2000 c.c. ammonia give
6000 c.c. hydrogen chloride + 1000 c.c. nitrogen;

and symbolized by him in this way:

$$3\phi + 2\phi_1 = 6\phi_2 + \phi_3.$$

By means of atomic symbols the reaction is thus represented:



It will at once be admitted that Brodie's equation does not show the qualitative aspect of the reaction; it claims, however, to be quantitatively accurate. Nevertheless this claim can only be strictly true if the volume relations given above are strictly true, and these can only be so if the gases are ideal gases, or similarly related to the ideal state of a gas.

As a matter of experience it has been found, for example, that at 0°C . and 760 mm. pressure, 1 volume of oxygen combines with 2.00288 volumes of hydrogen to form water, and there is no doubt that careful measurements of the volumes of chlorine and ammonia which react at any chosen temperature and pressure would show a similar deviation from the simple law of volumes of Gay-Lussac.

Now such deviation is bound to be recorded in any symbolic

presentation which is supposed to record the facts, and to be independent of theory; and thus Brodie's equation, showing simple volumetric relations between four different species of gas is certainly inaccurate. No such objection, however, can be urged against an equation made up of atomic symbols; for the theory that molecules of chlorine and ammonia interact as the equation shows, is entirely in accord with all known facts.

M. A. Nacquet criticized Sir Benjamin Brodie's Calculus, and pointed out, among other things, that by means of it nitrogen, chlorine, and potassium are represented as compound bodies, while others, such as mercury, are simple. And, whilst admitting its value as a means of applying algebra to chemistry, Nacquet offered upon it the following remarks, which subsequent experience has proved to be justified:

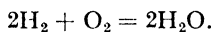
" Even if we do not take into consideration the extreme difficulty that there is in replacing one notation by another, and the momentary confusion introduced by it into science, a confusion which ought not to be permitted unless the change offers an undeniable advantage, we should oppose the immediate adoption of Sir B. C. Brodie's notation, because it seems to us to open the door to a crowd of suppositions more considerable than those it aims at eliminating, and because, from the point of view of the arrangement and anticipation of facts, it does not provide us with the means of dispensing with those atomic speculations which, without being intimately connected with the existing notation, may nevertheless be joined to it, and cannot in any case be adapted to the notation of Sir B. C. Brodie."

It may be noticed here that a modern attempt to reduce the atomic theory to the level of a working hypothesis, with the reality of which chemists are not immediately concerned, was made by W. Ostwald in his *Grundlinien der anorganischen Chemie* (English translation by Findlay as *The Principles of Inorganic Chemistry*, Macmillan, 1902), in his Faraday lecture, delivered before the Chemical Society on 19th April, 1904, and in a later book, *The Fundamental Principles of Chemistry* (translated by H. W. Morse, Longmans, 1909).

Ostwald showed that the conception of elements and compounds, and the laws of chemical combination, could be deduced from the principles of chemical dynamics; and, therefore, he regarded the atomic hypothesis rather as an "aid to representation" than a picture of reality. Thus he said that so far as the laws of chemical

combination were concerned there was a possibility, but not a certainty that the atomic hypothesis was true. Ostwald, therefore, chose to speak of combining and molar weights rather than of atomic and molecular weights. He was willing, nevertheless, to employ the atomic symbols of Berzelius for his combining and molar weights. Thus in *The Principles of Inorganic Chemistry*, p. 146, he said:

“A molar weight of hydrogen and oxygen each contains two combining weights of the elements; we must, accordingly, write:



From such an equation we can, at the same time, from the meaning of a molar weight, tell the volume ratios of the reacting gases. The present example shows directly that one volume of oxygen and two volumes of hydrogen yield two volumes of water-vapour.”

One is bound to respect this agnostic attitude of Ostwald towards the atomic theory. Yet for more than a hundred years chemists have believed in the reality of atoms; and their faith has been fully justified by modern knowledge of the natural world, which shows the atom, not indeed as an individual speck of matter, but as an individual entity which may be rightly represented by a symbol.

The Beginnings of Constitutional Formulæ.—We have now told the story of the evolution of chemical formulæ to the threshold of modern times. Henceforward we may take the empirical formulæ of elements and compounds for granted, and concern ourselves only with the newer problems of constitution.

We have first to witness the overthrow of dualism, and the growth of unitary views regarding the structure of chemical compounds; and then the development of the doctrine of types, which was the forerunner of the theory of valency.

Berzelius himself found a difficulty in applying his dualism to every compound. We have seen that he divided H^+Cl^- and N^+H_4^- into base and acid thus: H^+Cl^- and N^+H_4^- . Now if hydrogen can be the basic part of one acid why not of all acids? Similarly potassium chloride was K^+Cl^- ; why, then, should not sulphate of potash be K^+SO_4^- rather than KO, SO_3 ? The fact is that while it is possible to divide oxy-salts into separate oxides, which may be called respectively base and acid, this cannot be done in the case of salts not containing oxygen.

Now Davy was of opinion that hydrogen was the essential constituent of all acids, and that the electrolysis of, say, potassium sul-

phate was satisfactorily explained by supposing the salt to be divided into K and SO^4 rather than KO and SO^3 .

Graham, as we have seen, discovered the three forms of phosphoric acid, and Liebig, after extending Graham's researches to other acids, formulated his theory of poly-basic acids, judging an acid to be poly-basic if it formed a compound salt with more than one basic oxide, as, for instance, Rochelle salt. Liebig then placed on record the following statement:

"Acids are particular compounds of hydrogen, in which the latter can be replaced by metals."

Such a view undermined dualism, and was opposed by Berzelius; nevertheless it soon gained general acceptance.

The difficulties of dualism may be illustrated by a formula taken from organic chemistry. Berzelius formulated acetic acid thus: $\bar{A} = \text{H}^6\text{C}^4\text{O}^3$. Whilst we may note that we owe the abbreviated symbol $\bar{A}$ to Berzelius, it is more important for us to understand that the formula $\text{H}^6\text{C}^4\text{O}^3$ represents what we now call acetic anhydride; for Berzelius's formula for silver acetate is $\bar{A}\text{gA}$, i.e. AgO , $\text{H}^6\text{C}^4\text{O}^3$, a compound, like all other oxysalts, of two oxides.

Now Gerhardt proposed to halve the atomic weights of silver and the alkali metals to make their oxides conform to the water type M^2O . So silver acetate became Ag^2O , $\text{H}^6\text{C}^4\text{O}^3$, or, adopting the unitary way of representing a salt: $\text{Ag}^2\text{H}^6\text{C}^4\text{O}^4$. Now this formula is divisible by two. Ought it to be so divided? Gerhardt observed that the amount of water and of carbon dioxide evolved by the decomposition of a molecular proportion of an organic compound according to the formulæ of the day, was never less than $2\text{H}^2\text{O}$ and 2CO^2 . This was an argument for halving organic formulæ in general; for, said Gerhardt, it would be strange if no reaction should give rise to a single molecule of water or of carbonic acid. Thus the formula for silver acetate became $\text{AgH}_3\text{C}_2\text{O}_2$, which is the present-day formula.* If, however, this formula is accepted, acetic acid itself becomes $\text{HC}_2\text{H}_3\text{O}_2$, and conforms to the general formula HX for a monobasic acid. Such a formula, however, is necessarily unitary; it cannot be made dualistic in the Berzelian sense. Thus was dualism further discredited.

Nevertheless, with the growth of organic chemistry, Berzelius attempted to formulate carbon compounds on a dualistic basis. As elements were the constituent units of inorganic compounds, so

* We will now lower the small figures and write formulæ in the usual way.

compound radicals were the constituent units of organic compounds.

At first Berzelius was of the opinion that since oxygen was absolutely electronegative, it must necessarily stand apart, so as to be balanced by one or more radicals in a compound; in other words that it could not form part of a compound radical. The work of Liebig and Wöhler *Upon the Radical of Benzoic Acid*, shook his faith in this doctrine.

In 1817 he wrote: "The application of what is known regarding the combination of the elements in inorganic nature to the critical examination of their compounds in organic, is the key by which we may hope to arrive at true ideas with respect to the composition of organic substances."

Therefore, just as in inorganic chemistry, metals and metalloids formed oxides which as bases and acids then combined together to form salts; so in organic chemistry radicals combined with oxygen as the first step towards the formation of more complex compounds.

Benzoyl, the radical brought to light by the researches of Liebig and Wöhler, was represented as the oxide of the complex $C_{14}H_{10}$, to ether was given the formula $(C_2H_5)_2O$; though alcohol was regarded as the oxide of a radical C_2H_6 . Liebig, who more truly considered alcohol as hydrated ether, represented a number of compounds in the following way on a dualistic basis:

Ether	..	..	..	$C_4H_{10}O$
Alcohol	..	..	..	$C_4H_{10}O \cdot H_2O$
Ethyl chloride	..	..	..	$C_4H_{10}Cl_2$
Ethyl iodide	..	..	..	$C_4H_{10}I_2$
Nitrous Ether	..	..	..	$C_4H_{10}O \cdot N_2O_3$
Benzoic Ether	..	..	..	$C_4H_{10}O \cdot C_{14}H_{10}O_3$

Attempts such as this to represent organic compounds as composed similarly to inorganic might succeed for a time; but we know that they must fail sooner or later, according to the progress of knowledge of organic chemistry. For a rapid glance at the field of this science, as it stands displayed to-day, is sufficient to show the great variety in the structure of organic compounds that exist, and the error of supposing that these compounds are all built on the same plan like a row of suburban villas rather than constructed with infinite variety like stately mansions. We realize quite well that our knowledge of the structure of inorganic compounds is not "the key by which we may hope to arrive at true ideas with respect to the composition of organic substances". Nevertheless, we must now trace the steps

which led to more adequate ideas regarding the structure of chemical compounds in general, and more particularly of organic compounds.

The field is immense, and we might well hesitate to set out on its exploration; but when we remember that our purpose is to trace the evolution of the methods of formulation of chemical compounds, and not to explore the whole field of chemistry, we shall find that our task is like the study of agricultural implements rather than of agriculture itself.

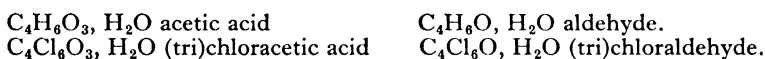
Let us first understand that, according to Berzelius, chemical compounds were electrically balanced systems; their formation depended upon the balancing of the electrical forces contained in their constituent atoms, and their destruction would consequently follow upon the upsetting of these forces. Nevertheless, it was early recognized that there might be more than one mode of union of certain atoms resulting in electrical equilibrium. In other words *Isomerism*, a term introduced by Berzelius himself, was known to occur. In 1823 Liebig showed that silver fulminate had the same composition as silver cyanate, in 1825 Faraday discovered butylene, a hydrocarbon having the same composition as ethylene; in 1828 Wöhler converted ammonium cyanate into urea, and in 1829 Berzelius himself showed that racemic and tartaric acids had the same quantitative composition.

Now the facts of isomerism did not necessarily contradict the dualistic hypothesis and the idea of electrical equilibrium. Other facts, however, which were now coming to light, created difficulty and were ultimately found to be irreconcilable with that hypothesis. Gay-Lussac had prepared cyanogen chloride, CNCl , from hydrocyanic acid, CNH ; Faraday had converted $\text{C}_2\text{H}_4\text{Cl}_2$ into C_2Cl_6 , and Liebig and Wöhler $\text{C}_6\text{H}_5\text{COH}$ into $\text{C}_6\text{H}_5\text{COCl}$; each transformation being a substitution of an atom of chlorine for one of hydrogen. It is clear that the dualistic hypothesis could not account for such transformations; for were not H and Cl electrically opposite? The existence of HCl as a stable compound proves them so to be. If then the formation of a chemical compound depends upon the equilibrium resulting from the neutralization of opposite electrical charges, such equilibrium is bound to be disturbed by the substitution of Cl for H. There is no doubt about the substitution. What, then, is to become of the theory?

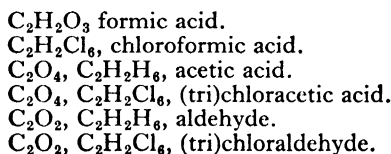
The work of Dumas, and the efforts of this chemist to show that organic compounds can be classified in types, is so important that it

must be referred to in some detail. Dumas protested against the idea that a chemical compound is necessarily composed of oppositely electrified parts which must be maintained in equilibrium. He preferred a mechanical to an electrical picture of the molecule. Indeed he compared a molecule with the solar system. The molecule might consist of atoms like planets without moons, or of radicals like planets with moons. If one planet of the solar system could be exchanged for another, that would not mean the destruction of the system, for the planets would adapt themselves to a new equilibrium to meet the modified conditions. So would it be with a chemical compound; the substitution of chlorine for hydrogen would mean some adjustment in the atomic system consistent with the disturbance caused by the substitution; but that was all. Dumas had a strong case, for had he not himself prepared trichloroacetic acid and found it to be similar to acetic acid? Dumas's planetary analogy wins our assent, so it remains to ask what types this chemist can show us.

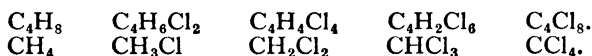
Trichloroacetic acid resembles acetic acid in this respect: that whilst an acetate yields marsh gas and a carbonate when decomposed by an alkali, a trichloroacetate similarly yields chloroform and a carbonate. Therefore the two acids belong to the same type. Aldehyde and chloraldehyde show similar relationships; and these four compounds are thus formulated: *



Here are some more of Dumas's formulæ chosen to show that there are sets of compounds built on the same type, or, as we should say containing the same radicals:



An analogy has been suggested between marsh gas and chloroform. Dumas gives the whole series, as conforming to the same type. His formulæ, with modern equivalents, are:



* The formulæ of Dumas had twice the number of carbon atoms because this chemist wrote $C = 6$. The correct formulæ are obtained by halving those given above.

To show further the connexion between organic and inorganic chemistry, Dumas sets out the following formulæ:

BaO	BaCl ₂	BaS	BaCy ₂ , &c.
SrO	SrCl ₂	SrS	SrCy ₂ , &c.
PbO	PbCl ₂	PbS	PbCy ₂ , &c.
CaO	CaCl ₂	CaS	CaCy ₂ , &c.
MgO	MgCl ₂	MgS	MgCy ₂ , &c.

He then arranges the following series of organic compounds analogous to the above:

$\begin{smallmatrix} C_8H_6 \\ H_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_8H_6 \\ Cl_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_8H_6 \\ O_3 \end{smallmatrix}$, &c.	
$\begin{smallmatrix} C_4H_2 \\ H_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_4H_2 \\ Cl_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_4H_2 \\ O_3 \end{smallmatrix}$,	$\begin{smallmatrix} C_4O \\ O_3 \end{smallmatrix}$, &c.
$\begin{smallmatrix} C_{28}H_{10} \\ H_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_{28}H_{10} \\ Cl_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_{28}H_{10} \\ O_3 \end{smallmatrix}$, &c.	
$\begin{smallmatrix} C_{24}H_6 \\ H_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_{24}H_6 \\ Cl_6 \end{smallmatrix}$,	$\begin{smallmatrix} C_{24}H_6 \\ O_3 \end{smallmatrix}$,	$\begin{smallmatrix} C_{24}H_4O \\ O_3 \end{smallmatrix}$, &c.

To modernize these formulæ divide the numbers of carbon atoms by 4, and of other atoms by 2. The formulæ thus represent C_2H_6 , CH_4 , $C_6H_5CH_3$, and C_6H_6 , and their derivatives.

These illustrations make it plain that what Dumas meant by an organic type was a certain substance containing a compound radical which yielded derivatives containing the same compound radical. For organic chemistry was the chemistry of compound radicals containing carbon; compound radicals which took the place of elements in inorganic chemistry. He claims that this manner of arranging organic compounds accords with a natural classification, and results in the creation of comparative chemistry.

The types of Dumas differ from those of Gerhardt and other chemists shortly to be described; but we must admit their value since they promoted the advancement of chemical science.

Further facts similar to those already recorded were being established by the work of Dumas. There is a story that this chemist, then resident in Paris, was consulted regarding an offensive odour emitted by candles burnt during a ball at the Tuileries; and that he discovered the odour to be that of hydrogen chloride, traceable to chlorine used to bleach the candles. Whether the story is true or not, it serves to draw attention to the facts of *substitution* which were carefully studied by Dumas. Notable examples of the substitution of chlorine for hydrogen in organic compounds observed by Dumas were the action of chlorine on turpentine and the formation of

chloral from alcohol. Consequently, in 1834, Dumas framed the following rule:

When a compound containing hydrogen is exposed to the dehydrogenizing action of chlorine, bromine, or iodine, it takes up an equal volume of chlorine, bromine, &c., for each atom of hydrogen that it loses.

The question of the relation of the chlorine derivative to the parent substance soon arose. Laurent was of opinion that the substitution of chlorine for hydrogen did not make much difference to the compound concerned; but Berzelius opposed this view. If such substitution must be admitted, it was incredible according to the electrochemical theory that the electrical difference between chlorine and hydrogen would not make itself felt when one element was substituted for the other in a compound. Meanwhile Dumas discovered chloracetic acid, which was recognized as still an acid, and so, true to *type*. This was the beginning of the type theory: the idea that the structure of a chemical compound has more influence in determining its properties than the elements of which it is composed. It was a unitary view of chemical compounds utterly opposed to dualism; and it may be expressed in the following way:

Every chemical compound forms a complete whole, and cannot therefore consist of two parts. Its chemical character is dependent primarily upon the arrangement and number of the atoms, and in a lesser degree upon their chemical nature.

The enunciation of this thesis forms so important a stage in the development of chemical theory that we may pause a little time to consider whether or how far it is true. We have marked the beauty of the electrochemical theory of Berzelius, and we have seen that it contains elements of truth when applied, as its author at first intended it to be applied, to inorganic compounds. Is this theory, then, to go for nothing; is dualism to be utterly displaced by unitarism? We know that a very large number of inorganic compounds, i.e. all electrolytes, which are acids, bases, and salts, are divisible into two parts; indeed that according to recent theory they consist always of two parts and never form a complete whole. It must be recognized, moreover, that the view which Dumas sought to apply to "every chemical compound" was developed in the study of organic compounds. Do organic compounds differ, then, so entirely from inorganic compounds? We know that this is not a proper question to ask; that the difference lies, not between organic and inorganic compounds, but between non-electrolytes and electrolytes; although it

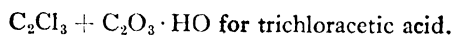
is true that organic compounds are generally non-electrolytes, and inorganic compounds electrolytes. The fundamental reason, however, why electrolytes consist of two parts, and non-electrolytes do not, has been adequately accounted for only in recent years, since the development of the electronic doctrine of valency, a discussion of which will be found later in this volume.

The dictum of Dumas, moreover, provokes a further question. Is it true to say that the chemical character of a compound depends primarily upon the arrangement and number of its atoms, and in a lesser degree upon their chemical nature? Consider CH_4 and CHCl_3 . These compounds are of the same type; but it cannot be said that they resemble one another either in physical or chemical properties. Or compare CH_4 with SiH_4 ; or else NCl_3 with BiCl_3 . None of these compounds resembles chemically the other with which it is paired. The truth is that although a good deal may be said for type in determining the nature of a chemical compound, there is also much to be said for the elements of which the compound consists. And it is simply common sense to suggest that the more atoms the molecule of a compound contains the less difference will the substitution of one atom for another make.

Berzelius attempted to defend his dualism against the rising tide of other views; that is to say, he attempted to construct dualistic formulæ for the new organic compounds which were being discovered. Thus he invented the following formulæ:

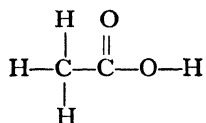


and

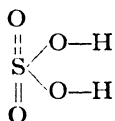


Nevertheless, although there was an admission of the principle of substitution in these formulæ, which itself went far to undermine dualism, this concession did not save the theory; for the growing doctrine of types was found to be so valuable an aid in the development of organic chemistry, that dualism was forgotten, and unitary views took the field. We are bound to regret that the truth in dualism was for a time forgotten with the error. For when graphic formulæ were developed with the use of bonds, these formulæ, which were a true aid in organic chemistry, were probably not so helpful in the inorganic branch of the subject. Indeed we may regret the attempt to represent the constitutions of many inorganic compounds by the use of bonds; for not only were these formulæ unsupported by facts, but they often misrepresented the facts.

For example, it may be a wise and true thing to represent acetic acid by the graphic formula:



although it is open to question whether the two oxygen atoms are really situated differently; but whether sulphuric acid should be represented by the graphic formula:



in which two of the oxygen atoms are shown bound to sulphur differently from the other two is another question. Indeed there seems no doubt that the four oxygen atoms in the sulphate radical are similarly disposed towards the sulphur atom, and therefore that the graphic formula for the acid which was long accepted by the orthodox as true, is untrue.

The discussion of such a subject as this, however, is an anticipation of what will appear later in this book. It is mentioned here only to enable us to say that if the truth that lay in dualism had not been thrown away with the error, recent views of the constitution of inorganic compounds might have been held earlier, and controversy perhaps avoided. For Davy held the view that a metallic sulphate was not $\text{M}_2\text{O}, \text{SO}_3$, but M_2, SO_4 ; and there is no doubt that this is a truer way of representing a metallic sulphate than $\text{SO}_2(\text{OM})_2$.

Although dualism as a theory disappeared, dualism as a convenient way of expressing analytical data survived. When a mineral carbonate or silicate is analysed the results show so much base, i.e. basic oxide such as CaO , K_2O , or Al_2O_3 , and so much carbon dioxide, CO_2 , or silica, SiO_2 . Indeed it would be difficult to express the composition of complex silicates in any other way. It is a singular fact, also, that popular names for well-known salts are dualistic in origin and form as, for example, sulphate of potash, nitrate of soda, carbonate of lime.

Now let us see how the theory of types became a valuable aid in the development of organic chemistry. First we must remember

that organic chemistry was the chemistry of compound radicals. This view was agreed to by Berzelius, and it was thus expressed by Dumas and Liebig: "Organic chemistry possesses its own elements, which sometimes play the part of chlorine or oxygen, sometimes that of a metal. Cyanogen, amidogen, benzoyl, and the radicals of ammonia, of the fats, and of alcohol and its derivatives, constitute the true elements of organic nature, while the simplest constituents, such as carbon, hydrogen, oxygen, and nitrogen, only appear when the organic substance is destroyed."

The difference between Berzelius and Dumas was that according to Berzelius the radicals were held together by electrical attraction, thus being either positive or negative, whilst according to Dumas they were held together in some more intimate way so as to form a whole not consisting of positive and negative parts.

In a letter addressed to Dumas in 1841 Graham made an ingenious attempt to harmonize electrochemical and unitary views of organic compounds. After all, he said, the atoms of elements in organic compounds must be held together by some force, and that force might well be electrical. If electrical, then some of the atoms must be electropositive and others to balance them electronegative. Let us, he said, place the symbols of the electronegative atoms above a line in the formula, and those of the balancing electropositive atoms opposite them below the line. Thus the following formulæ were devised:

water $\frac{\text{O}}{\text{H}}$, carbonic acid $\frac{\text{O}_2}{\text{C}}$, hydrate of potash $\frac{\text{OO}}{\text{KH}}$, carbonate of potash $\frac{\text{O}_2\text{O}}{\text{CK}}$, olefiant gas $\frac{\text{H}_4}{\text{C}_4}$ or $\frac{\text{H}_2\text{H}_2}{\text{C}_2\text{C}_2}$, ether $\frac{\text{H}_5\text{O}}{\text{C}_4}$, alcohol $\frac{\text{H}_5\text{OO}}{\text{C}_4\text{H}}$.

Some of these formulæ may then be taken as types; for example:

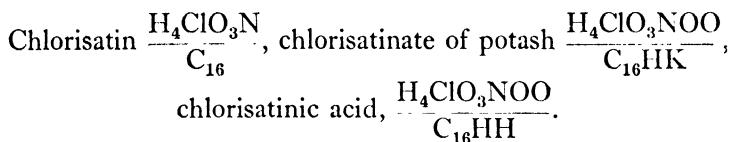
Olefiant gas type $\frac{\text{H}_4}{\text{C}_4}$: chloride of carbon $\frac{\text{Cl}_4}{\text{C}_4}$.

Ether type $\frac{\text{H}_5\text{O}}{\text{C}_4}$: ethyl chloride $\frac{\text{H}_5\text{Cl}}{\text{C}_4}$, ethylene dichloride $\frac{\text{H}_4\text{Cl}_2}{\text{C}_4}$.

Alcohol type $\frac{\text{H}_5\text{OO}}{\text{C}_4\text{H}}$: acetic acid $\frac{\text{H}_3\text{O}_3\text{O}}{\text{C}_4\text{H}}$, chloracetic acid $\frac{\text{Cl}_3\text{O}_3\text{O}}{\text{C}_4\text{H}}$.

Aldehyde type $\frac{\text{H}_3\text{OO}}{\text{C}_4\text{H}}$: chloral $\frac{\text{Cl}_3\text{OO}}{\text{C}_4\text{H}}$.

This method might even be applied to complex organic compounds, e.g. chlorisatin dissolves in potash, forming a salt, from which chlorisatinic acid can be liberated, thus:

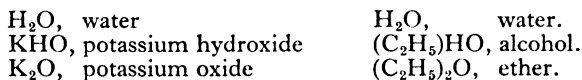


It will be observed that the addition of atoms to the numerator is compensated for by an equal number of atoms added to the denominator.

This scheme came to nothing; but what is worth remembering about it is the fact that it was the outcome of an attempt to account for the forces joining atoms together in organic compounds. It is only within recent years that chemists have desired to solve this problem. They have been so immersed in the problem of constitution, i.e. the problem as to how the atoms are joined together by means of bonds, that they have scarcely stayed to inquire what stuff bonds are made of. Now, as we shall see, this problem is being attacked.

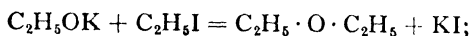
It did not follow from the unitary view that simple inorganic compounds could not stand as types of organic compounds, in which radicals might take the place of elements. Indeed it was by taking such compounds as types that progress was made in organic chemistry.

It will be seen, however, that the simple compounds taken as types are for the most part unitary rather than dualistic in nature. Let us start with water, according to the ideas of Laurent. Water can have its hydrogen displaced in two stages by, say, potassium, with the formation of potassium hydroxide and oxide respectively. An organic radical might, however, take the place of potassium; let us say ethyl, which was now recognized as C_2H_5 . Thus the following analogies appear:

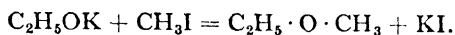


This is the beginning of the system of types, which was developed by Gerhardt, and generally goes by his name. Its value is manifest, and it will be interesting to follow it further. It was Williamson, however, who first introduced the *water type*, and wrote thus about

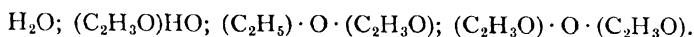
it: "The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of." This view was justified, for Williamson himself made discoveries by its aid. Thus he prepared diethyl ether by this reaction:



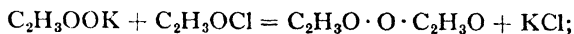
and by substituting methyl for ethyl iodide obtained, and so discovered, a mixed ether thus:



(C_2H_5) and (CH_3) are basic radicals; why should not acidic radicals take their place? Such a suggestion is inconsistent with dualism, but not with the theory of types. Thus acetic acid is ($\text{C}_2\text{H}_3\text{O}$)HO; why should not the radical ($\text{C}_2\text{H}_3\text{O}$) displace the radical (C_2H_5) so as to produce another series of compounds according to the water type thus:



The third of these compounds is ethyl acetate, acetic ether, or acetic ester, as we now call it. What is the fourth compound? It is the acetic analogue of K_2O . It was unknown; but from this simple analogy Williamson said that it ought to exist. How then might it be prepared? Ethyl ether is analogous to K_2O , and therefore its manner of preparation suggests how the new compound might be prepared; thus acetic oxide might be prepared in the same manner as ethyl oxide. What an opportunity for scientific discovery this simple suggestion made by Williamson offered! Gerhardt tried the experiment; i.e. he heated together potassium acetate and acetic (acetyl) chloride, thus:



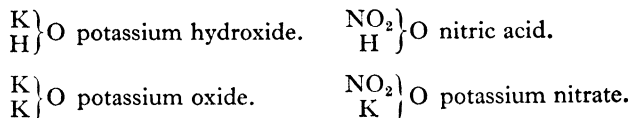
and obtained a colourless, volatile, liquid, boiling at 137°C .

Thus was acetic anhydride discovered. Upon this and other discoveries of the same kind Liebig made this comment: "The discovery of the anhydrides of the organic acids is one of the most brilliant that has been made of late."

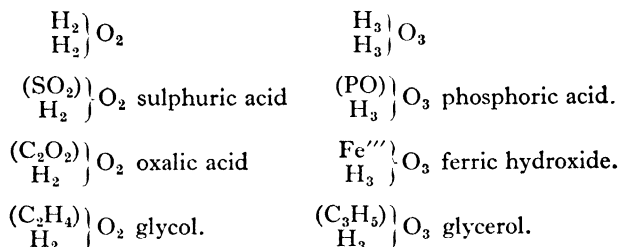
If a theory is to be judged by its fruits, the theory of types was a veritable tree of knowledge.

62 SYMBOLS AND FORMULÆ IN CHEMISTRY

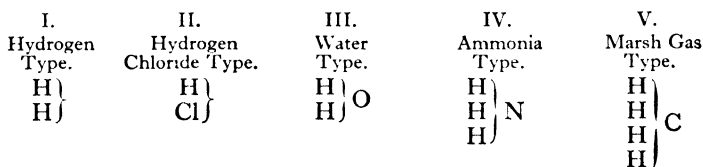
The water type was further extended to include inorganic oxyacids and salts thus:



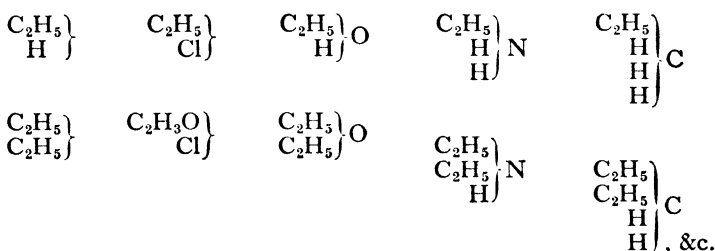
Also double and triple water types were introduced, as for example:



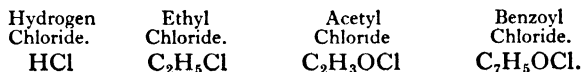
Gerhardt's types were four in number; and to these Kekulé added a fifth, the marsh-gas type.



For example:

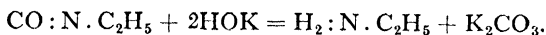


There was perhaps no need for the hydrogen chloride type. It does not seem to differ essentially from the hydrogen type, since each atom in this type may be exchanged for any other equivalent atom or radical. It served, however, to draw attention to the following interesting series of chlorides:

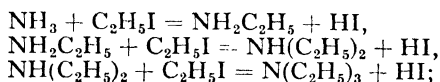


The story of the *ammonia type* is an interesting one.

In 1830 Dumas discovered oxamide, and Liebig concluded that this and other amides contained the radical NH_2 , and thus conceived the idea of substituted ammonias. In 1849 Wurtz prepared ethylamine by a reaction which we now represent thus:

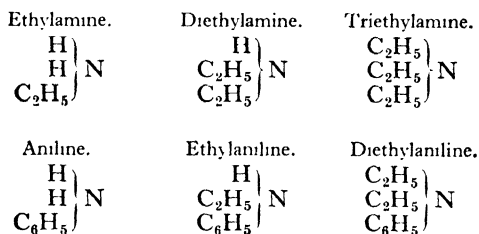


Hofmann, too, prepared a succession of substituted ammonias by replacing hydrogen by alkyl groups in the following reactions:



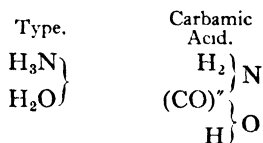
and by his study of aniline and its derivatives provided further examples of compounds of the ammonia type.

So Wurtz, who at first was inclined to regard amines as compounds of ammonia with hydrocarbons according to the dualism of Berzelius, was enabled to realize that a number of substituted ammonias had been obtained; as for example:



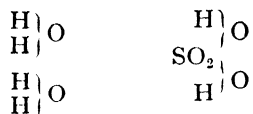
“It was thus,” said Wurtz, “that the ammonia type was created.”

It did not long remain desirable or possible to refer all known compounds to one or other of the above simple types. In 1853 Gerhard referred the amino-acids to an ammonia + water type, as for example, carbamic acid:

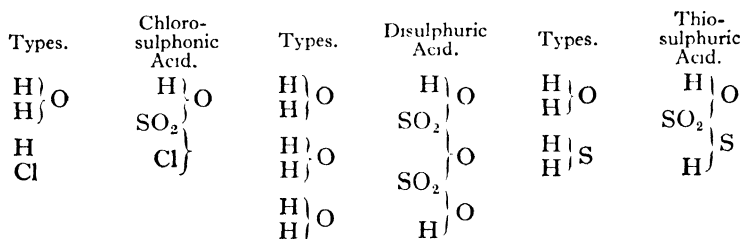


a conception, however, which resulted from the idea of polyatomic radicals introduced by Williamson in 1851; for this chemist had represented sulphuric acid as derived from two molecules of water

by the displacement of two hydrogen atoms, one from each water molecule by the diatomic radical SO_2 , thus:

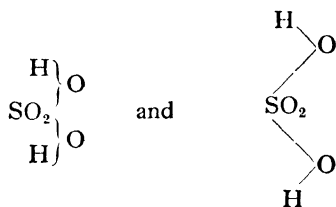


So the way was prepared for condensed and mixed types, of which the following are other examples:



The term "conjugation" had been employed by Laurent and Gerhardt in 1848 to designate the union of two bodies with the elimination of water, as in the reaction $\text{C}_2\text{H}_6\text{O} + \text{H}_2\text{SO}_4 = \text{C}_2\text{H}_5\text{SO}_4 + \text{H}_2\text{O}$; but this idea was shown by Kekulé to be superfluous when he wrote: "A union of several molecules of the types can only occur when, by the entrance of a polyatomic radical in place of two or three atoms of hydrogen, a cause is furnished for the holding of these molecules together."

From our vantage ground we can see in this sentence the beginning of the idea of valency, and the chemical bond. Indeed it is very easy to assume that the two formulæ for sulphuric acid:



mean the same thing. Perhaps as much as this should not be said; yet we see in Kekulé's idea a departure from Gerhardt's types and the idea of conjugation in the direction of modern constitutional formulæ.

The formulation of the *marsh-gas type* by Kekulé in 1854 coincided with the birth of the valency idea. Marsh gas CH_4 , chloro-

form CHCl_3 , chloropicrin CNO_2Cl_3 , were seen to belong to the same type; but it is in the following words that the existence of the type is most clearly shown by Kekulé: "If we look at the simplest compounds of this element—i.e. carbon— CH_4 , CH_3Cl , CCl_4 , CHCl_3 , COCl_2 , CO_2 , CS_2 and CHN , we are struck by the fact that the quantity of carbon which is considered by chemists as the smallest amount capable of existence—the atom—always binds four atoms of a monatomic or two of a diatomic element, so that the sum of the chemical units of the elements combined with one atom of carbon is four. We are thus led to the opinion that carbon is tetratomic." This sentence, however, contains much more than a justification of the marsh-gas type. In it the author speaks of the binding of the atoms, i.e. of atomic bonds; and he says that carbon is tetratomic, i.e. quadrivalent, as we should say.

Now to find the origin of valency we must retrace our steps a little way.

Kolbe and Edward Frankland were friends and colleagues; and both were at first disciples in the school of Berzelius, that is to say, both regarded organic compounds as formed by the copulation of radicals. Thus in 1848, and again in 1856, Kolbe formulated acetic acid as $(\text{C}_2\text{H}_3)\text{C}_2\text{O}_3$, HO , having an anhydride $(\text{C}_2\text{H}_3)\text{C}_2\text{O}_3$, some of whose oxygen was replaceable by Cl or NH_2 , forming the acid chloride $(\text{C}_2\text{H}_3)\text{C}_2\text{O}_2\text{Cl}$ or amide $(\text{C}_2\text{H}_3)\text{C}_2\text{O}_2\text{NH}_2$. The idea of copulation seems vague; yet it can be traced back to the electrochemical theory of Berzelius which attributed the formation of a chemical compound to the electrical attraction between its oppositely charged parts. This view, however, was irreconcilable with the type theory of Gerhardt, as indeed the authors concerned were not slow to point out.

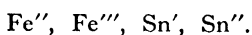
In 1852 Frankland published his researches upon the organo-metallic compounds; and at the same time showed that his views upon the constitution of organic compounds had undergone a change. Consider the compounds: SnO , SnO_2 , $\text{Sn}(\text{C}_2\text{H}_5)_2$, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{O}$. Tin can combine with one or two atoms of oxygen; it can also combine with two ethyl groups in place of an oxygen atom; but, having combined with two such groups it can afterwards combine with one but not two atoms of oxygen. Thus the tin atom has a certain *saturation capacity* which cannot be exceeded. Now according to the radical theory the power of metals to combine with oxygen is not diminished by their copulation with radicals; but the results of Frankland proved the contrary.

The passage in which Frankland set forth his new views is so important that it may be quoted. "When the formulæ of inorganic compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony, and arsenic, especially, exhibit the tendency of these elements to form compounds containing 3 or 5 atoms of other elements; and it is in these proportions that their affinities are best satisfied: thus in the ternary group we have NO_3 , NH_3 , NI_3 , NS_3 , PO_3 , PH_3 , PCl_3 , SbO_3 , SbH_3 , SbCl_3 , AsO_3 , AsH_3 , AsCl_3 , &c.; and in the 5-atom group, NO_5 , NH_4O , NH_4I , PO_5 , PH_4I , &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms."

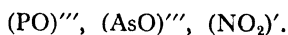
Frankland saw in the new view a means of reconciling the radical and type theories. He said: "The formation and examination of the organo-metallic bodies promise to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable; for, whilst it is evident that certain types or series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electrochemical character of its single atoms, and not merely upon the relative position of those atoms."

The idea of valency thus expressed by Frankland was generally accepted by chemists, and Kolbe was favourably disposed towards it. It was not, however, until the distinction between equivalent, atomic, and molecular weights was recognized through the work of Gerhardt and Laurent, and the principles of atomic weight determination had been established by Cannizzaro, that the valencies of the elements could be ascertained.

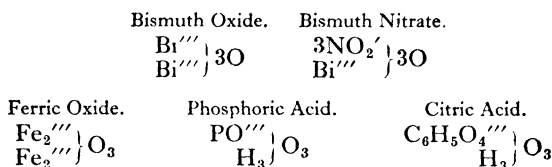
Meanwhile the seed sown by Frankland was beginning to grow. Odling represented the valencies of the elements by dashes attached to their atomic symbols, thus:



The valencies of radicals were also represented similarly thus:



The method of Odling is further illustrated by the following formulæ:



It is plain from these symbols and formulæ that the atomic weights of tin and iron had half their present value. It is interesting to notice here the comparison between inorganic and organic compounds, and to find the triple water type again employed.

In connexion with the employment of dashes to represent units of valency the following formulæ of Gerhardt may be cited.*

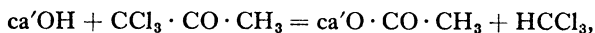
Atomic Formulæ.		Equivalent Formulæ.
H'Cl	Hydrochloric acid.	H'Cl
Na'Cl	Sodium chloride.	Na'Cl
S''Cl ² .	Sulphur chloride.	s'Cl
Sn''Cl ² .	Stannous chloride.	stn'Cl
Sn'''Cl ⁴ .	Stannic chloride.	sn'Cl
P'''Cl ³ .	Phosphorous chloride.	p'Cl
Si'''Cl ⁴ .	Silicon chloride.	si'Cl
Bi'''Cl ³ .	Bismuth chloride.	bi'Cl
C'''Cl ⁴ .	Carbon chloride.	c'Cl
Fe'Cl.	Ferrous chloride.	Fe'Cl
Ffe'''Cl ³ .	Ferric chloride.	ffe'Cl
Hhg'Cl.	Mercurous chloride.	Hhg'Cl
Hg'Cl.	Mercuric chloride.	Hg'Cl
Pt'Cl.	Platinous chloride.	Pt'Cl
Pt''Cl ² .	Platinic chloride.	pt'Cl

This table shows symbols for atoms and for equivalents of certain elements forming chlorides. It will be seen that different symbols are used for different equivalents of the same element, e.g. stn and sn, Fe and ffe, Hhg and Hg, though it may be asked why small initial letters are sometimes but not always employed for the symbols of equivalent weights.

Such symbols have almost entirely disappeared; they were probably too elaborate and cumbrous to last. An interesting relic or reintroduction of equivalent symbols, however, is seen in some textbooks of organic chemistry. For example, in Cohen's

* *Vide Watt's Dict.*, 1882, Vol. II, art. "Equivalents".

Theoretical Organic Chemistry (1902) we find the following equation:

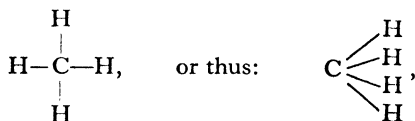


and in a later edition (1923) the following:



$\text{ca} \left(= \frac{\text{Ca}}{2} \right)$ being written to save doubling the equation.

Let us return to a pregnant phrase used by Kekulé in a passage quoted above (p. 65). This chemist says that an atom of carbon always binds four atoms of a monatomic element. Binding is by means of bonds. Concerning bonds two questions may be asked: first, of what do bonds consist? second, how may bonds be represented symbolically? To the first question the only answer that has ever been given is the answer of Berzelius, that atoms are held together by electrical attraction. It is true that this attraction has been called chemical affinity, and much labour has been expended in estimating the relative values of different affinities; but of the qualitative nature of affinity itself the measurements tell us nothing. Concerning the representation of bonds symbolically, however, there is much to be said; not, indeed, concerning the bond itself, but about the development of its use. The bond itself is represented simply by a stroke of the pen, by a straight line drawn short or long according to convenience. Thus the bonds binding the atoms of hydrogen to the atom of carbon in marsh gas are represented thus:



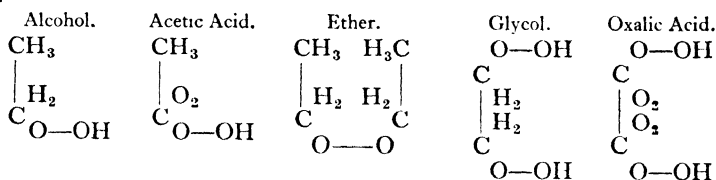
for so far as the stage of chemical theory we are considering at present is concerned there is no difference between these two formulæ. It was not Kekulé, however, who first used the bonds with which we are now so familiar, but his less illustrious contemporary Couper.* Nevertheless Kekulé had a clear mental conception of the facts which were represented symbolically by Couper. For, having come to the conclusion that carbon was "tetraatomic", Kekulé said: "In the cases of substances which contain several atoms of carbon, it must be assumed that at least some of the atoms are in the same way held in the compound by the affinity of carbon, and that the carbon atoms attach themselves to one another, whereby

* Archibald Scott Couper, of Kirkintilloch.

a part of the affinity of the one is naturally engaged with an equal part of the affinity of the other. The simplest, and consequently the most probable case of such an attachment of two carbon atoms is that in which one unit of affinity of the one atom is united with one of the other. Of the 2×4 affinities of the two carbon atoms, two are therefore employed in holding the two atoms themselves together; six thus remain over which can be held by atoms of other elements."

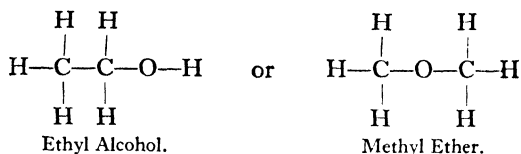
Thus Kekulé accounted for the compound C_2H_6 , or more generally for the series of paraffin hydrocarbons C_nH_{2n+2} . It may be asked why, having gone so far, Kekulé did not write graphic formulæ as we know them. It would seem so simple and obvious a thing to make diagrams on paper of carbon compounds with their atoms bound together. Kekulé, however, was a follower of Gerhardt; and Gerhardt's types were not graphic formulæ; they were not meant actually to represent chemical constitution, they were not architect's plans of the molecules of matter.

So it was left for a man, who looked at things from a different point of view, to make the actual plans. Here are Couper's formulæ for some well-known compounds; they differ from ours because Couper wrote $O = 8$, so that two oxygen atoms appear in place of one.



Thus the first graphic or constitutional formulæ appeared in 1858; and the great use these formulæ have been in the study of chemical constitution can be seen by turning over the pages of any standard textbook of organic chemistry. Such formulæ are less frequent in inorganic chemistry because the problem of constitution is less important there. This branch of chemical science deals with the comparatively simple compounds which all the elements form with one another, whereas organic chemistry has to do with the compounds of only a few elements, but is greatly concerned with the way in which their atoms are joined together. For example, the formula $CaCO_3$ expresses all that a formula need express to indicate the identity of the compound it represents; but the formula C_2H_6O does not convey sufficiently precise information; for there are two compounds whose composition is expressed by this formula,

and it is necessary to know which of the two is intended. That is expressed by one of the two following formulæ which show constitution by means of bonds.

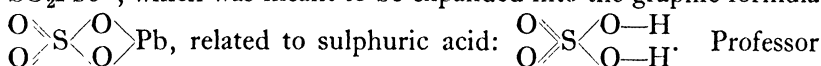


It is true that the formula CaCO_3 is sometimes expanded thus: $\text{Ca} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}=\text{O}$, in accordance with the bivalency of calcium and oxygen and the quadrivalency of carbon, carbonic acid itself being represented by the formula $\begin{array}{c} \text{H}-\text{O} \\ | \quad \diagdown \\ \text{H}-\text{O} \end{array} \text{C}=\text{O}$. There is, however, an objection to these "graphic formulæ"; it is that calcium carbonate as calc-spar is shown by them to be constituted differently from sodium nitrate NaNO_3 , with which it is isomorphous, NaNO_3 being represented thus: $\text{Na}-\text{O}-\text{N} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$. Such formulæ for inorganic salts are now being abandoned; it would have been more scientific not to have used them, for a constitutional formula should represent only constitution for which there is experimental foundation. Nevertheless inorganic chemists have allowed their fancies to play freely around this subject. Given the atomic composition of compounds and the valencies of their constituent atoms, it becomes an interesting exercise to build formulæ with bonds to hold all the atoms together. So alumina, in which aluminium is trivalent, and oxygen bivalent, can be represented thus: $\text{Al} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{Al}$, or thus,

$\text{O}=\text{Al}-\text{O}-\text{Al}=\text{O}$. There seems nothing to choose between these formulæ, and they tell us nothing which is not expressed by the formula Al_2O_3 .

In his Presidential Address to the Chemistry Section of the British Association at Edinburgh in 1892, Professor Herbert M'Leod gave an account of the views regarding structural formulæ of inorganic compounds which were held at that date. Referring to lead sulphate, he said that Berzelius wrote its formula as PbO, SO_3 , and Hofmann as PbSO_4 ; and that whilst Gerhardt, by doubling the atomic weights of oxygen and sulphur, wrote Pb_2SO_4 , Cannizzaro, by doubling also

the atomic weight of lead, brought the formula back again to PbSO_4 . Nevertheless Frankland, we are reminded, wrote the formula $\text{SO}_2\text{Pbo}''$, which was meant to be expanded into the graphic formula

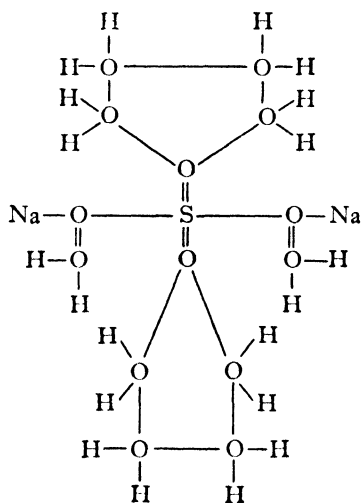
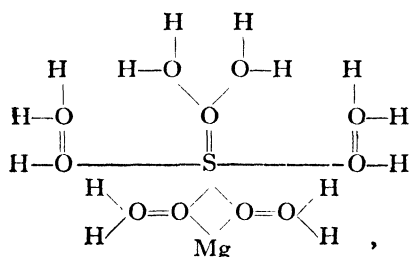


Professor M'Leod approves of these formulæ, not only because they satisfy Dalton's requirement, in 1835, that a formula represent the weights of the elements present, and also their arrangement, but also because they show the four oxygen atoms not all in the same condition.

Until recently these graphic formulæ and the views expressed by M'Leod were acceptable to chemists. Now, however, there is reason to believe that the four oxygen atoms in the sulphate radical are symmetrically placed with reference to the sulphur atom, and the formula for a sulphate therefore takes a different guise, which will appear later.

M'Leod then discusses "residual affinity" by which it is supposed that water of crystallization is retained in hydrated salts in a state of "molecular combination". "Oxygen may be tetrad," he says, and then proceeds to develop graphic formulæ for hydrated salts:

Magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{OH}_2$ or $\text{SOH}_2\text{Mgo}'' \cdot 6\text{OH}_2$; and sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{OH}_2$; are represented thus:



Even alum may be expressed by an "appalling formula" which covers half a page, and need not be reproduced. "By a little stretching of the imagination," says Professor M'Leod, "no doubt graphic

formulæ might be made for all crystalline salts, but they would be perfectly artificial." Agreed!

As a matter of fact, however, it is now possible to construct a graphic formula for alum which is not perfectly artificial, but is based upon actual knowledge of the space disposition of the atoms in a crystal of this substance, as revealed by X-ray spectrography.*

Historically, however, this is a digression, so let us return to the subject of structure and bonds in organic chemistry. Couper introduced bonds in 1858, and Butlerow, about this time was the first to speak of "the structure of a chemical compound" whilst Erlenmeyer used the term "constitution" in the same sense. Butlerow, indeed, in 1860, recognized that the future work of the chemist lay in discovering "the nature and manner of mutual union of the atoms in the molecule".

When, in 1859, Kekulé began to construct graphic formulæ, he did not employ Couper's bonds, but drew pictures of atoms of different sizes to represent different degrees of "atomicity" or valency, which recall the symbols of Dalton. Here are examples of Kekulé's formulæ at that time:



We find, however, that by 1865 Kekulé had adopted bonds; and the extent to which structural formulæ were in use at this date may be judged from the contents of a lecture delivered by Dr. A. W. Hofmann before the Royal Institution in April, 1865.

Hofmann first gives a number of cases of what are called "homologous series" in which a number of compounds in a series are characterized by a common difference. Here are some examples:

Increment of Oxygen

Hydrochloric acid	..	HCl.
Hypochlorous acid ..	..	HCl + O = HClO.
Chlorous acid ..	..	HCl + 2O = HClO ₂ .
Chloric acid	..	HCl + 3O = HClO ₃ .
Perchloric acid ..	..	HCl + 4O = HClO ₄ .
Olefiant gas	..	C ₂ H ₄ .
Aldehyde	..	C ₂ H ₄ + O = C ₂ H ₄ O.
Acetic acid	..	C ₂ H ₄ + 2O = C ₂ H ₄ O ₂ .
Glycollic acid ..	..	C ₂ H ₄ + 3O = C ₂ H ₄ O ₃ .

*Vide *Crystallography and Practical Crystal Measurement*, by A. E. H. Tutton, Macmillan & Co., 1922, Vol. I, p. 678.

Increment of Nitrogen

Hydride of ethyl	C_2H_6 .
Ethylamine	$C_2H_5 + HN = C_2H_7N$.
Ethylene diamine	$C_2H_4 + 2HN = C_2H_8N_2$.
Vinyl triamine	$C_2H_3 + 3HN = C_2H_9N_3$.

Increment of Carbon

Hydrocarbons

Marsh gas	CH_4 .
Hydride of Ethyl	$CH_3 + CH_3 = C_2H_6$.
Hydride of Propyl	$CH_3 + 2CH_2 = C_3H_8$.
Hydride of Butyl	$CH_3 + 3CH_2 = C_4H_{10}$.

Alcohols

Methylic alcohol	CH_3O .
Ethylic alcohol	$CH_3O + CH_2 = C_2H_6O$.
Propylic alcohol	$CH_3O + 2CH_2 = C_3H_8O$.
Butylic alcohol	$CH_3O + 3CH_2 = C_4H_{10}O$.
Amylic alcohol	$CH_3O + 4CH_2 = C_5H_{12}O$.

Acids

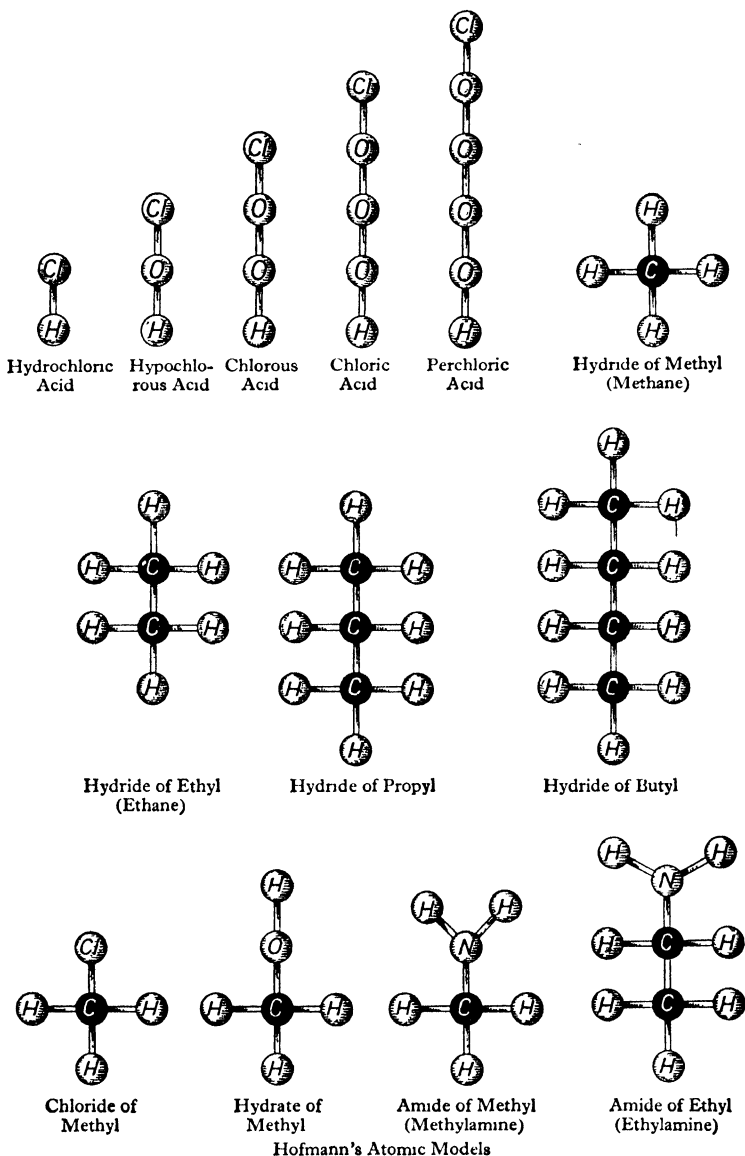
Formic acid	CH_2O_2 .
Acetic acid	$CH_3O_2 + CH_2 = C_2H_4O_2$.
Propionic acid	$CH_3O_2 + 2CH_2 = C_3H_6O_2$.
Butylic acid	$CH_3O_2 + 3CH_2 = C_4H_8O_2$.
Valeric acid	$CH_3O_2 + 4CH_2 = C_5H_{10}O_2$.

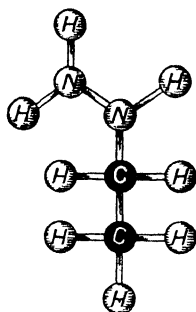
He then draws attention to the fact that the actual increments in these cases are O, NH, CH_2 ; and explains these by pointing out that two units of attraction are needed to join each O, N, or C atom to its neighbours, and that an atom or atoms of hydrogen are held by the remaining units which each atom possesses. Thus since the atoms of O, N, and C possess in all 2, 3, and 4 units of attraction or valencies, respectively the oxygen atom has none, the nitrogen atom one, and the carbon atom two units to spare to combine with hydrogen.

It is interesting to record that for this lecture Hofmann constructed atomic models with croquet balls of different colours, and provided with arms to represent units of attraction. His models, corresponding with some of the above formulæ, are reproduced on the following page.

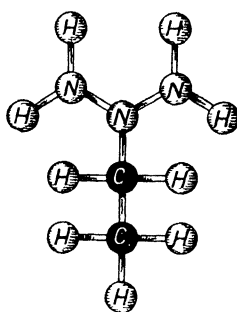
The models for the oxyacids of chlorine represent constitutions which we do not accept to-day, but they are the only representation possible if the idea that chlorine is necessarily univalent and oxygen bivalent is adhered to. The chain formulæ for paraffin hydrocarbons of the type C_nH_{2n+2} , which were devised by Kekulé, are acceptable,

and so is the formula for ethylamine. The formula attributed to ethylene-diamine, however, represents the constitution of ethylhydrazine, and the so-called vinyl-triamine is unknown. Attention must be drawn to the formula attributed to olefiant gas, in which one carbon atom has two and the other no bonds to spare. In

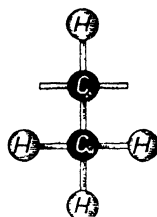




Ethylene-diamine



Vinyl-triamine



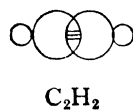
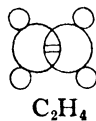
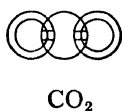
Olefiant Gas

Hofmann's Atomic Models

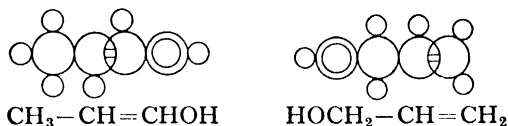
consequence of this, Dutch liquid must be represented as ethylidene and not ethylene chloride, an error due to the fact that the conception of the carbon double bond had not yet been reached. The same fact, indeed, is the reason for the ethylene-diamine formula, which does not permit an NH_2 group to be attached to each of two carbon atoms.

It is remarkable that Hofmann could construct these models and not realize that, being bi-dimensional, they fell short of depicting the true structures of molecules which are themselves necessarily tri-dimensional. The time for stereochemistry, however, had not yet arrived, though it was not far off; thus further developments waited on further needs.

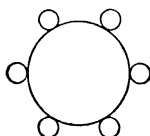
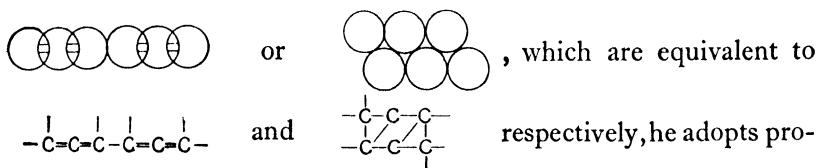
Attention may here be drawn to a very interesting publication by Loschmidt, entitled *Chemische Studien* (Vienna, 1861), which Anschütz has brought to light.* This little treatise contains 368 graphic formulæ, of which 121 are those of aromatic substances. The symbols used by Loschmidt recall Dalton's symbols; thus a small circle stands for an atom of hydrogen, a larger circle for an atom of carbon, two concentric circles for an atom of oxygen, and so on. What is more significant, however, is that when formulæ are made from these symbols, double and triple bonds appear, as the following examples show:

* *Berichte*, 1912, 35, 539.

Isomerism, too, is recognized between "propylene oxide" and allyl alcohol, although the former is incorrectly formulated, thus:



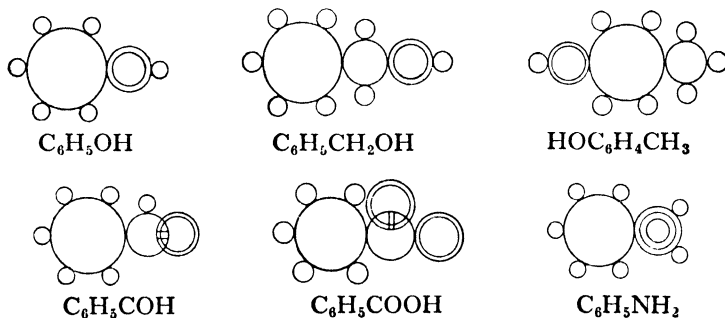
More far-reaching, however, are the speculations of Loschmidt upon the "phenyl series". After discussing whether C_6 should be



so comparing C_6H_6 with CH_4 , which has been formulated as

It therefore appears that Loschmidt developed a ring formula for benzene about four years before Kekulé independently conceived the same idea. Moreover, Loschmidt's ring is equivalent to the benzene hexagon without double bonds, which is in common use, since both leave in abeyance the question of the disposition of the fourth carbon valency.

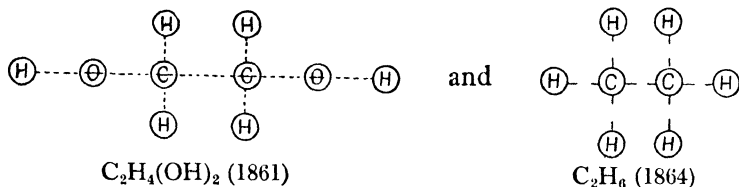
The following formulæ show that Loschmidt had a clear idea of the constitutions of certain well-known benzene derivatives:



It is interesting to notice that the isomerism of benzyl alcohol and cresol was recognized.

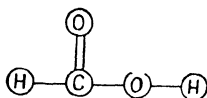
The formulæ of Loschmidt, however, suffer from the same disability as those of Dalton; for, even if they had become widely known, their cumbrous character would have prevented their general use. Chemists cannot be drawing circles for their formulæ.

In 1861 Crum Brown* used bonds similar to those introduced by Couper, but also reverted to circles containing initial letters as atomic symbols. Thus glycol and ethane were represented respectively as:



It will be observed that during the three years intervening between the first and second of these formulæ the barred symbols C and O, meaning two atoms when $\text{C} = 6$, $\text{O} = 8$, have given place to ordinary symbols because $\text{C} = 12$ and $\text{O} = 16$, and also that the dotted lines have given place to "bonds", although these are not joined together between the elements. Concerning these formulæ Crum Brown wrote: "An atom is represented by its usual symbol surrounded by a circle with as many lines proceeding from it as the atom contains equivalents. When equivalents mutually satisfy one another the two lines representing the equivalents are made continuations of one another."

Two years later he wrote continuous lines between the symbols, and in 1868 constructed the following formula for formic acid:

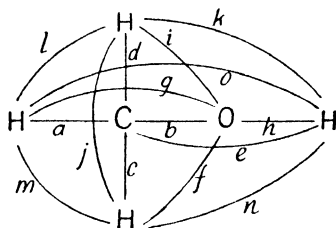


about which he said: "The structural formula of formic acid indicates first, that the four carbon equivalents form one atom, the four oxygen equivalents two atoms, and the two hydrogen equivalents two atoms; secondly, that these equivalents are united in pairs, thus: co, co, co, ch, ho, but it does not in any way indicate (and we do not know) what is the potential of each of these pairs—that is,

* *Vide Walker, J. Chem. Soc., 1923, 123, 942.*

how much energy would be required to separate the equivalents from each other. We know that this potential depends upon the structure, and we can to a certain extent trace the nature of this dependence, but as yet we cannot express the potential numerically, and till we can do that we do not fully know the constitution."

This passage contains several interesting points. First it is to be noted that small letters are used for the equivalents of elements whose atoms are represented by the corresponding capitals. This has been met with before. Second, that the "bond" represents a link, but does not represent its strength; the idea of force enters qualitatively but not quantitatively into the bond. Third, that every atom within a molecule attracts and holds every other atom, so that the attractive forces are not localized to the lines between the atoms. Sir James Walker,* who draws attention to this idea, suggests that the lines of force binding together the atoms of so simple a molecule as methyl alcohol can be represented thus:



Such a formula, however, is of no practical utility.

The condition of chemical notation about this time is further shown in a paper by Frankland.†

Frankland gives the following formulæ:

Alcohols.	Ethers.	Fatty Acids.	Aldehydes.	Ketones.
$\text{C} \begin{cases} \text{CH}_3 \\ \text{H} \\ \text{H} \\ \text{OH} \end{cases}$	$\text{C} \begin{cases} \text{CH}_3 \\ \text{H} \\ \text{H} \\ \text{OC}_2\text{H}_5 \end{cases}$	$\text{C} \begin{cases} \text{CH}_3 \\ \text{O} \\ \text{OH} \end{cases}$	$\text{C} \begin{cases} \text{CH}_3 \\ \text{O} \\ \text{H} \end{cases}$	$\text{C} \begin{cases} \text{CH}_3 \\ \text{O} \\ \text{CH}_3 \end{cases}$
Ethylic Alcohol.	Ethylic Ether.	Acetic Acid.	Acetic Aldehyde.	Acetone.

It is seen that by the recognition of the quadrivalency (tetra-atomicity) of carbon, the univalency of the groups CH_3 and OC_2H_5 , and the bivalency of oxygen, these formulæ agree with those accepted at the present day, except that instead of containing bonds

* *Loc. cit.*

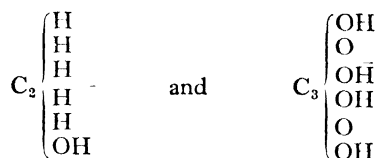
† "Contributions to the Notation of Organic and Inorganic Compounds", *J. Chem. Soc.*, 1866, 19, 372.

they are made to conform to the marsh-gas type in which a bracket is employed. Concerning the first formula Frankland writes: "This is a true representation of the internal arrangement of the atoms composing alcohol, not, indeed, of their relative positions with regard to each other in space, but of the mode in which they are held together."

Then after discussing the possibility of vibratory motion of hydrogen and other atoms within the molecule, Frankland continues: "The formula proclaims, however, that all these atoms of hydrogen must remain exclusively under the domination of their respective carbon and oxygen atoms so long as the compound continues to exist."

These sentences are significant, because they adumbrate the problems of stereochemistry and tautomerism which arose later.

After suggesting that ethylic alcohol and mesoxalic acid could equally well be written in this way:



respectively, he points out that C_3 is an "octadic" group which might be written thus: $\text{C}-\text{C}-\text{C}$; but in view of the unwieldy character of such drawn-out formulæ, he suggests the following abbreviations for "compound radicles": Me = methyl, Et = ethyl, All = allyl, Pr = propyl, Bu = butyl, Ay = amyl; and, adopting the marks of atomicity proposed by Odling, the following: $\text{Me}'' = \text{CH}_2$ or methylene, $\text{Me}''' = \text{CH}$ or formyl, $\text{Et}'' = \text{C}_2\text{H}_4$ or

ethylene. So "acetic ether" is abbreviated to $\text{C O} \begin{matrix} \text{Me} \\ \text{OEt} \end{matrix}$. Then there

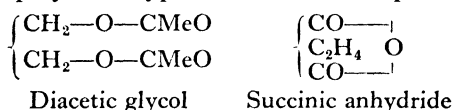
follow other abbreviations, as, for example:

Name.	Atomic Formula.	Symbol.
Hydroxyl ..	HO	Ho
Methoxyl ..	CH_3O	Meo
Hydrosulphyl ..	HS	Hs
Ammonium ..	NH_4	Am
Ammonoxyl ..	NH_4O	Amo
Amidogen ..	NH_2	Ad
Potassoxyl ..	KO	Ko
Zincoxyl ..	$\text{Zn}''\text{O}_2$	Zno''

The utility of some of these abbreviations may be questioned; for example, why write Ho for HO? The answer is that the single symbol saves brackets; thus FeHo_3 can be written for $\text{Fe}(\text{HO})_3$, and similarly K_4FeCy_6 for $\text{K}_4\text{Fe}(\text{CN})_6$. Few, however, of these symbols have survived. Me and Et are sometimes used for CH_3 and C_2H_5 , as well as Ph for C_6H_5 , and Am for NH_4 ; the atomic symbols seem, however, to be preferred in cases where they are not much more trouble to write.

When employing abbreviated or other symbols to build up formulæ, Frankland places the element of highest valency, "the grouping element", to the left, and prints it in heavy type. Thus the formula for sulphuric acid becomes $\overset{\text{vi}}{\text{SO}}_2\text{Ho}_2$, in which the sulphur being sexivalent, as we now say, has six bonds, four of which are employed to bind the two oxygen atoms, and one to bind each of the two Ho radicles. The idea of valency units appearing or disappearing in pairs is also developed here. Thus nitrogen is quinquivalent in $\overset{\text{v}}{\text{N}}\text{H}_4\text{Cl}$, trivalent in $\overset{\text{iii}}{\text{N}}\text{H}_3$, and univalent in $\overset{\text{i}}{\text{O}}\text{N}_2$; and the explanation follows that "one or more pairs of bonds belonging to an atom of the same element can unite, and, having saturated each other, become, as it were, latent."

The bond, as we know it, is seldom used by Frankland. "In rare cases," he employs a "hyphen" as, for example:

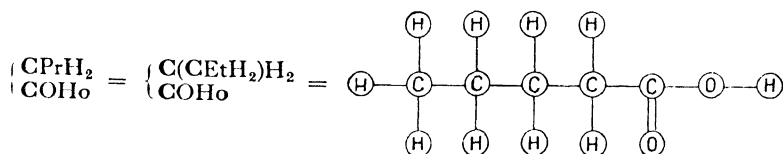


The bracket, indeed, serves wherever possible instead of bonds to unite atoms together. Here are some of Frankland's constitutional formulæ for organic and inorganic compounds:

Name.			Formula.
Ethylamine	..	..	NEtH_2
Acetamide	..	..	$\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CONH}_2 \end{array} \right.$ or $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{COAd} \end{array} \right.$
Urea	..	..	$\left\{ \begin{array}{l} \text{NH}_2 \\ \text{CO} \\ \text{NH}_2 \end{array} \right.$ or $\text{N}_2(\text{CO})'\text{H}_4$
Glycerin	..	..	$\left\{ \begin{array}{l} \text{CH}_2\text{Ho} \\ \text{CHHo} \\ \text{CH}_2\text{Ho} \end{array} \right.$
Benzylic alcohol	..	..	$\left\{ \begin{array}{l} \text{C}(\text{C}_6\text{H}_5)\text{H}_2 \\ \text{CH}_2\text{Ho} \end{array} \right\}$ normal
Cresylic alcohol	..	..	$\left\{ \begin{array}{l} \text{CH}_3 \\ \text{C}(\text{C}_6\text{H}_5) \text{ HHo} \end{array} \right\}$ secondary

Name.		Formula.
Cupric sulphate ..	..	$\text{SO}_2\text{Cu}''$
Potassic sulphate ..	..	SO_2Ko_2
Microcosmic salt ..	..	POHoAmoNao
Zincic nitrate ..	..	$\left\{ \begin{array}{c} \text{NO}_2\text{O} \\ \text{Zn} \\ \text{NO}_2\text{O} \end{array} \right\}$ or $\text{N}_2\text{O}_4\text{Zno}''$ (Thus $\text{o}'' = 2\text{O}$)
Potassic chromate ..	..	CrO_2Ko
Dipotassic dichromate ..	..	$\left\{ \begin{array}{c} \text{CrO}_2\text{Ko.} \\ \text{O} \\ \text{CrO}_2\text{Ko.} \end{array} \right.$

That these formulæ may be expanded by the use of bonds, however, is shown by Frankland and Duppa,* who expand the formula for valeric acid thus:



So we arrive at the same manner of formulation as was adopted by Crum Brown about the same time.

It will be agreed that these formulæ manifest a deep knowledge of chemical constitution, expressed in ways which do not differ widely from ours. The heavy type symbols of Frankland do not, however, seem to have been adopted by other chemists.

**J. Chem. Soc.*, 1867, 20, 113.

CHAPTER III

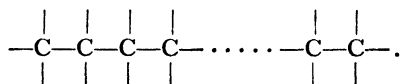
The Theory of Structure

To trace further the development of graphic formulæ we must return to Kekulé. Intended by his father to be an architect, he became indeed the architect of the chemical molecule. The story of the origin of the "Structur theorie" has often been told.* Kekulé had daydreams of chains of carbon atoms like snakes "whirling in a giddy dance"; then one of the snakes "seized hold of its own tail"; and that was the origin in the mind of Kekulé of the benzene ring!

Kekulé believed in the fixity of valency, so that the carbon atom was always "tetraatomic", or quadrivalent, as we should say. When a compound contains two atoms of carbon united together, then "one unit of affinity of one carbon atom is combined with one unit of affinity of the other. Of the 2×4 units of affinity of the two carbon atoms, two are used up in holding the two atoms together; there therefore remain six which may be held in combination by atoms of other elements. In other words the group C_2 is hexatomic."

Thus by using the "bonds" of Couper, or the atom models of Crum Brown, the graphic formula of the C_2 group becomes $\begin{array}{c} | & | \\ -C & -C- \\ | & | \end{array}$,

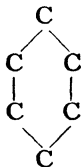
and it is but a step from this to the recognition that the group C_n has $n(4 - 2) + 2 = 2n + 2$ units of affinity. This step was taken by Kekulé, who must therefore be credited with the conception of the carbon chain, or "carbon skeleton", which is characteristic of the paraffin hydrocarbons and their derivatives:



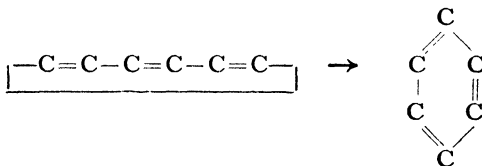
It was such a chain, twisting like a snake, that Kekulé saw in

* *Vide* Japp, Kekulé Memorial Lecture, *J. Chem. Soc.*, 1898, 73, 99.

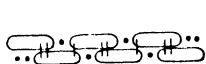
his daydream, and when the snake swallowed its own tail, like the snake in the old Egyptian hieroglyph, this was the result:



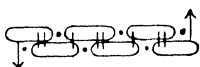
the benzene ring or hexagon. Six carbon atoms in a chain, however, would contain 14 free valencies, and when the chain became a ring there would still be 12. So to use up 6 free valencies Kekulé assumed the 6 carbon atoms of a chain to be joined by single and double bonds alternately, thus: —C=C—C=C—C=C— , and so by converting this into a closed chain he produced the familiar benzene hexagon, with single and double bonds alternating, thus:



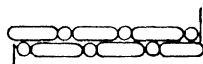
‘From this *closed chain*,’ said Kekulé, “all substances usually designated as aromatic compounds are derived.” The actual way in which Kekulé first constructed his formulæ for aromatic substances is not, however, so familiar. Here are some of his formulæ for benzene and its derivatives, as they were published in 1865.*



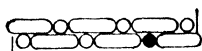
Chaîne ouverte



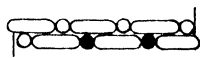
Chaîne fermée



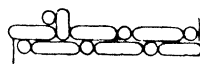
Benzine



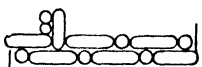
Benzine chlorée



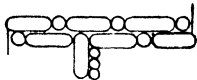
Benzine bi-chlorée



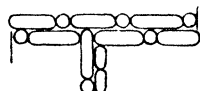
Alcool phénolique



Aniline



Toluol

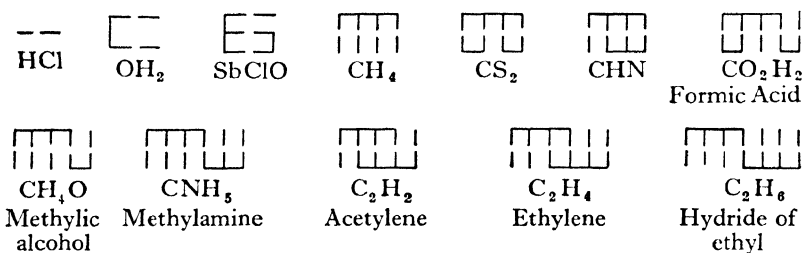


Acide benzoïque

* Bull. Soc. Chim., 1865, 3, 108.

Such formulæ serve to show the development of Kekulé's ideas. They are quaint, but accord with the ring formula, with alternating single and double bonds, given a little later. Like other formulæ representing or derived from models they are, however, unsuitable for general use.

Formulæ which resemble those of Kekulé in principle are to be found in an article on "Classification" by G. C. Foster in an old edition of Watts's *Dictionary* (1883), Vol. I, p. 1010. The signs used are — , $\square$, $\square\square$, or $\square\square\square$, according to whether the valency of an element is 1, 2, 3, or 4. The following illustrations will make plain their use.



Such formulæ are ingenious and useful in showing ideas of constitution, but they are not chemical formulæ because they do not contain atomic symbols. For example, $\begin{array}{c} \square\square\square \\ | \quad | \quad | \\ \text{H} \quad \text{H} \end{array}$ signifies the same

mode of union as $\text{H}—\text{C}=\text{C}—\text{H}$, but the latter formula has the advantage of showing what chemical atoms are united together.

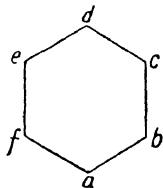
A year later Kekulé abandoned the picturesque formulæ given above, and in a paper on "The Constitution of the Aromatic Compounds",* began to develop the theory and formulation of the benzene ring, now so familiar to organic chemists.

"In all aromatic substances," said Kekulé, "a common nucleus may be assumed: it is the closed chain C₆A₆ (in which A denotes an unsaturated affinity). The six affinities of this nucleus may be satisfied with six monatomic elements. They may also, wholly or at least in part, be satisfied by one affinity of polyatomic elements, the latter necessarily bringing with them other atoms into the compound, thus producing one or more *side-chains*, which in their turn may be lengthened by the addition of other atoms." It follows

* *Ann.*, 1866, 137, 129.

from this that a substituent atom or radical may appear either in the nucleus or the side chain; and so we arrive at formulæ, as, for example, for benzyl alcohol and cresol, which are essentially similar to those given by Loschmidt, viz. $C_6H_5 \cdot CH_2 \cdot OH$ and $HO \cdot C_6H_4 \cdot CH_3$. Kekulé went further than this, however, for he recognized the possibility of isomerism of position when two or more substituents took the place of hydrogen atoms in the benzene nucleus. Concerning the structure of benzene, therefore, he formulated the following two hypotheses:

First Hypothesis.—The six carbon atoms of the benzene molecule formed a symmetrical ring with six equivalent positions for hydrogen or other atoms or groups. So was created the benzene hexagon with its angles lettered thus:



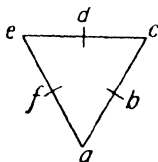
Thence it appeared that isomerism would occur amongst derivatives, as, for example, when bromine atoms were successively substituted for atoms of hydrogen. According to Kekulé the following brom-substitution products should be possible:

1. Monobrombenzene : 1 modification.
2. Dibrombenzene : 3 modifications: *ab*, *ac*, *ad*.
3. Tribrombenzene : 3 modifications: *abc*, *abd*, *ace*.
4. Tetrabrombenzene : 3 modifications: (as for 2).
5. Pentabrombenzene : 1 modification.
6. Hexabrombenzene : 1 modification.

Also the following tri-substituted derivatives, such as dibrom-nitrobenzenes, should be possible.

1. Positions *abc* : $C_6H_3BrBr(NO_2)$.
 $C_6H_3Br(NO_2)Br$.
2. Positions *abd* : $C_6H_2(NO_2)HBr_2$.
 $C_6H_2BrH(NO_2)Br$.
 $C_6H_2BrHBr(NO_2)$.
3. Positions *ace* : $C_6HBrHBrH(NO_2)$.

Second Hypothesis.—The six carbon atoms of the benzene molecule were so arranged that the hydrogen atoms occurred in two sets of three, as shown in the following scheme:



The three hydrogen atoms at the angles *a*, *c*, and *e* of the triangle

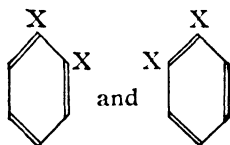
were more accessible than those at *b*, *d*, and *f*, which were farther within the molecule. This scheme introduced inequality among the hydrogen atoms, and consequently provided for a larger number of isomers, as, for example:

1. Monobrombenzene : 2 modifications: *a*, *b*.
2. Dibrombenzene : 4 modifications: *ab*, *ac*, *bd*, *ad*.
3. Tribrombenzene : 6 modifications: *abc*, *bcd*, *abd*, *abe*, *ace*, *bd $\bar{f}$* .
&c.

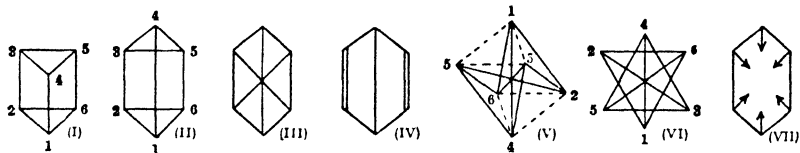
Kekulé added that to decide which of the different formulæ for benzene was to be adopted it was necessary to prepare and study as many substitution products as possible; and especially to endeavour to trace the cause of their difference to their mode of formation.

Which of the two hypotheses was the more probable did not, however, long remain in doubt. There was never any evidence of the existence of two monosubstituted derivatives of benzene, and Kekulé himself soon became the advocate of the chemical equivalence of all the hydrogen atoms; a fact, however, which was proved by Ladenburg in researches extending from 1869 to 1874.*

Nevertheless Kekulé's benzene hexagon indicated isomerism among (ortho) di-derivatives when the quadrivalency of carbon was shown by alternate double and single bonds. Thus positions 1 : 2 differ from positions 1 : 6 on account of the double bond between the 1 : 6 positions; and the two di-derivatives indicated are:



To meet this difficulty Ladenburg,† then working in Kekulé's laboratory, advocated the prism formula (I), the projection of which (II) had been put forward by Claus in 1867.



Claus himself, however, preferred the diagonal formula (III), whilst formula (IV), originally advocated by Dewar,‡ was also

* *Vide* Kipping's Ladenburg Memorial Lecture, *J. Chem. Soc.*, 1913, 103, 1882.

† *Ber.*, 1869, 2, 140, 272.

‡ *Proc. Roy. Soc.*, Edin., 1866-7, 84.

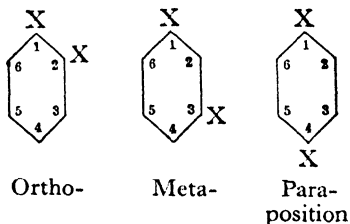
favoured by Wichelhaus. It is noteworthy that Kekulé, discussing various formulæ,* introduced among other figures the octahedron, which was brought forward again by Thomsen † in the form shown in figure (V), and was used later with such success by Werner in his co-ordination theory of valency.

Mention may be made here of Ladenburg's star formula (VI), which is equivalent to the prism formula (I) and its projection (II), since bonds from any point join three other points similarly in all three formulæ; also of the centric formula (VII) which is a modification of the diagonal formula (III) of Claus. This formula was first proposed by Armstrong ‡ to overcome the difficulty of the double bonds in Kekulé's formula, and afterwards adopted by Baeyer;§ the idea underlying it being that of the 24 units of valency of the 6 carbon atoms of the benzene molecule, the 6 which are not otherwise required act towards the centre "so that the affinity may be said to be uniformly and symmetrically distributed".

Kekulé himself, however, had realized the defect in his original hexagonal formula with its alternating single and double bonds, and the consequence that positions 2 and 6 differed in relation to position 1. Therefore he had suggested || the hypothesis that each double bond oscillates to and fro from one end, like a pendulum, so that during unit time these bonds are not localized in 3 positions only, but are distributed equally round the hexagon. Dynamically this idea is conceivable, but whether the valencies of carbon atoms behave in such fashion is another question.

Into the merits of these different benzene formulæ it is not possible to enter fully here. In spite of its defects Kekulé's hexagonal formula has been retained for general use, the anomalous distribution of its double bonds being generally overlooked, or avoided by the use of the hexagon of single bonds.

The nomenclature of the isomeric di-derivatives of benzene we owe to Körner, a pupil of Kekulé. Thus Körner introduced the terms ortho-, meta-, para- (o, m, p), though it appears that the 1, 2 derivative was at first called meta, and the 1, 3 derivative ortho. As is well-known, the accompanying formulæ represent a long-established system of nomenclature.



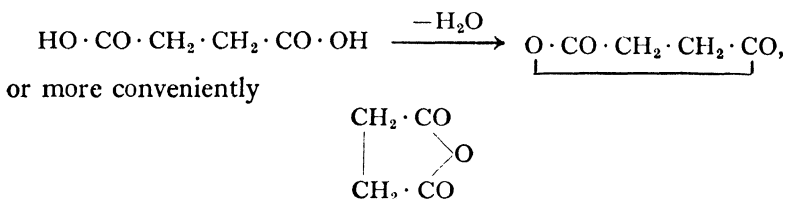
* *Ber.*, 1869, 2, 362.
§ *Ann.*, 1888, 245, 118.

† *Ber.*, 1886, 19, 2944.
|| *Ann.*, 1872, 162, 77.

‡ *J. Chem. Soc.*, 1887, 51, 264.

It is rather strange that the continuous lines employed by Crum Brown in 1868 to represent equivalents or units of valency in graphic formulæ were not always afterwards employed by chemists. Thus from 1870 till 1886 the sign $— \cdot —$ appears in the *Berichte*, and Claus, in a formula for mesitylene,* employs the combination $— \cdot —$ for the double bond in the benzene nucleus. In the middle of 1886 these broken lines were replaced by the continuous lines which had been used throughout by the London Chemical Society.

The use of a dot instead of a line, as, for example, in the formula $\text{CH}_3 \cdot \text{CO} \cdot \text{OH}$, is for convenience only, and has no significance, since the magnitude of a bond is not represented by the length of the line which symbolizes it. Consider succinic acid and its anhydride:



Thus lines or dots are employed indifferently, and in a way most convenient to formulate the compound.

Attention may now be drawn to the devices adopted to formulate isomeric hydrocarbons and their derivatives. When the number of carbon atoms in a chain exceeds two the differences between the positions of these atoms are often indicated by the use of Greek letters, which begin indifferently from either end of the chain.

The following illustrations may be given:

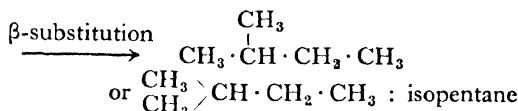
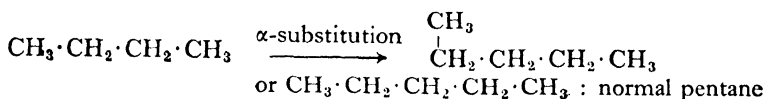
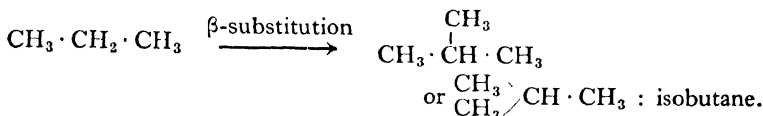
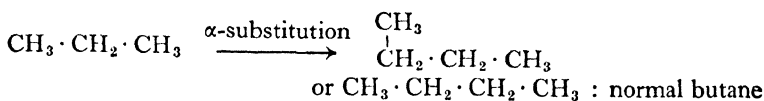
$\text{CH}_3 \cdot \text{CH}_3.$	$\text{CH}_3 \cdot \text{CH}_2\text{Cl}$	chloroethane
$\alpha \quad \beta \quad \alpha$ $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	α -chloropropane
	$\text{CH}_3 \cdot \text{CHCl} \cdot \text{CH}_3$	β -chloropropane
$\alpha \quad \beta \quad \beta \quad \alpha$ $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3.$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	α -chlorobutane
	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CH}_3$	β -chlorobutane
$\alpha \quad \beta \quad \gamma \quad \beta \quad \alpha$ $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	α -chloropentane
	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CH}_3$	β -chloropentane
	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{CH}_3$	γ -chloropentane

Di-derivatives are thus represented:

$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CH}_2\text{Cl}$	$\alpha\beta$ -dichloropentane
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	$\alpha\gamma$ -dichloropentane
$\text{CH}_3 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	$\alpha\delta$ -dichloropentane, &c.

* *Ber.*, 1870, 3, 180.

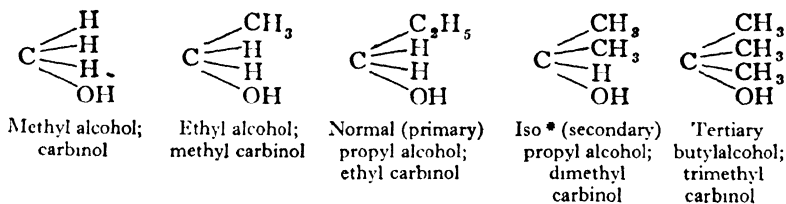
The same kind of formulation serves to represent branch chains, as, for example, by the substitution of a methyl group for a hydrogen atom:



Isobutane can also yield the isomeric pentane $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{CH}_3 \end{array} \begin{array}{c} \diagdown \\ \text{CH}_3 \end{array}$, which is tetramethylmethane.

As the number of carbon atoms increases the number of isomers is greatly multiplied: but these examples are enough to show the purpose of lettering the carbon atoms in hydrocarbons. An alternate way of expressing isomeric hydrocarbons is to regard them all as derivatives of methane. Thus normal butane is propyl methane; $\text{H}_3\text{C} \cdot \text{C}_3\text{H}_7$, and isobutane trimethyl methane $\text{HC}(\text{CH}_3)_3$; normal pentane is butyl methane, and isopentane ethyl dimethyl methane.

Reference to the methane type is, however, more useful in the case of the alcohols in accordance with Kolbe's carbinol theory, e.g.:



Greek lettering is also employed in formulating derivatives of carboxylic acids and other derivatives of hydrocarbons, but in this

* The prefix *iso* is not systematic, since it indicates only an isomer of the normal compound.

case the lettering proceeds from one end of the carbon chain to the other.

Compare, for example, propane and normal propionic acid, $\overset{\alpha}{\text{CH}_3} \cdot \overset{\beta}{\text{CH}_2} \cdot \overset{\alpha}{\text{CH}_3}$ and $\overset{\beta}{\text{CH}_3} \cdot \overset{\alpha}{\text{CH}_2} \cdot \text{COOH}$;

From propionic acid two hydroxypropionic acids are derived: $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ and $\text{CH}_2(\text{OH}) \cdot \text{CH}_2 \cdot \text{COOH}$, which are respectively α - and β -hydroxypropionic acid. Similarly from normal butyric acid: $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, three hydroxyacids, α , β , and γ , are derived; and from the iso-acid $\begin{matrix} \beta & \text{CH}_3 \\ & \diagup \\ \beta & \text{CH}_3 \end{matrix} \text{CH} \cdot \text{COOH}$, two, viz. α and β , hydroxyisobutyric acids.

Even more systematic are the Geneva nomenclature and formulation, which are the findings of an International Congress held at Geneva in 1892, viz.:

Names of saturated hydrocarbons end in -ane.

Names of hydrocarbons with one double bond end in -ene.

Names of hydrocarbons with two double bonds end in -diene, &c.

Names of hydrocarbons with one triple bond end in -ine, &c.

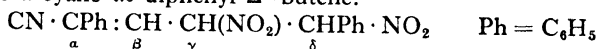
Alcoholic, aldehydic, ketonic, and carboxylic groups are indicated by the suffixes: -ol, -al, -one, -oïc, respectively.

Carbon atoms in chains are numbered consecutively from the left. The following are examples of this formulation and nomenclature:

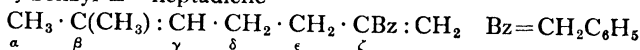
$\overset{1}{\text{CH}_3} - \overset{2}{\underset{\text{CH}_3}{\text{CH}}} - \overset{3}{\text{CH}_2} - \overset{4}{\text{CH}_2} - \overset{5}{\text{CH}_3}$	2-methyl pentane
$\text{CH}_3 - \text{CH}_2 - \text{CHOH} - \text{CH}_2 - \text{CH}_3$	3-pentanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CHO}$	4-methyl-5-pentanal
$\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$	2-pentanone
$\text{CH}_3 - \text{CH}_2 - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \text{CH}_2 - \text{COOH}$	3-ethyl-5-pentanoïc.
$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_3$	2-pentene
$\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_3$	3-pentine
$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$	1 : 3-pentadiene
$\text{CH}_2\text{OH} - \text{CH}_2 - \text{CHOH} - \text{CH}_2 - \text{CH}_3$	1 : 3-pentane-diol.
$\text{HOOC} - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{COOH}$	3-methyl-1 : 5-pentane dioïc.

This kind of formulation and nomenclature is found in modern textbooks; nevertheless Greek letters are frequently used instead of numbers. Moreover, the capital Δ is employed to signify the double bond, as the following names and formulæ show:

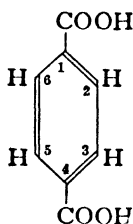
$\gamma\delta$ -dinitro- α -cyano- $\alpha\delta$ -diphenyl- Δ^a -butene.



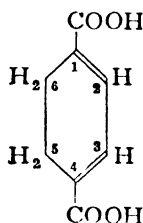
β -methyl- ζ -benzyl- $\Delta^{\beta\zeta}$ -heptadiene



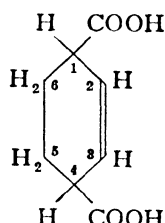
The sign Δ is similarly used in closed chain or cyclic compounds, such as benzene derivatives, as, for example:



(Δ^{1-3-5}) terephthalic acid
1:4 benzene dicarboxylic acid or benzene-p-dicarboxylic acid

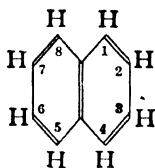


(Δ^{1-3}) dihydro-terephthalic acid

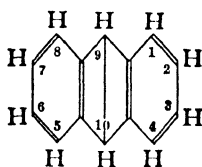


(Δ^2) tetrahydro-terephthalic acid

The formulæ for naphthalene (E. Erlenmeyer, Sr.) and anthracene (Graebe and Liebermann) are:

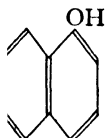


Naphthalene

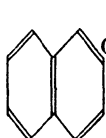


Anthracene

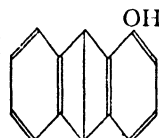
These formulæ are justified because they show, in the case of naphthalene, the existence of two monoderivatives, e.g. α and β



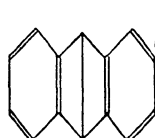
α -naphthol



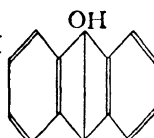
β -naphthol



α -anthrol



β -anthrol

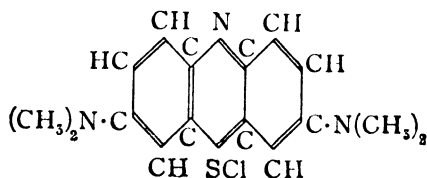
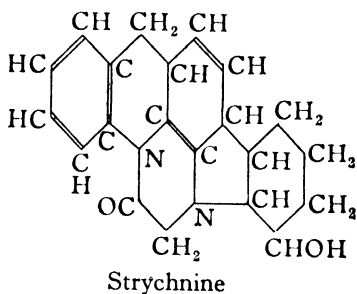
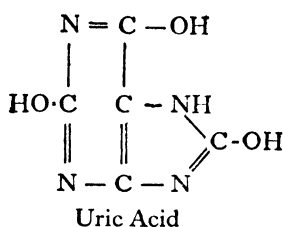
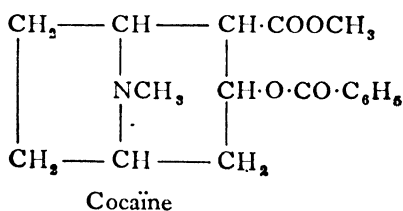
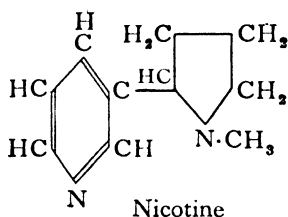
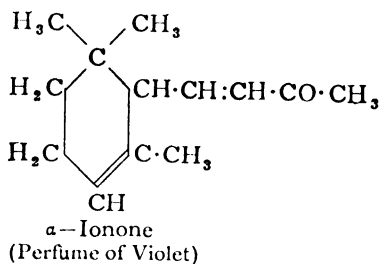
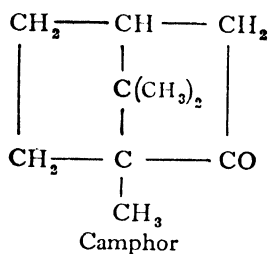


γ -hydroxyanthracene
(anthranol)

naphthol; and in the case of anthracene 3 monoderivatives, e.g.

α and β anthrols, and the hydroxy-compound known as anthranol.

Constitutional formulæ constructed of carbon chains, of homo-cyclic or hetero-cyclic rings—that is, rings composed entirely of carbon atoms, or of carbon atoms together with other atoms, such as those of nitrogen, oxygen, or sulphur—or of combinations of these different forms, often assume great complexity, especially when they represent natural products, or synthetic products such as dyestuffs. Here are a few examples of such complex formulæ for some well-known substances:



Methylene Blue

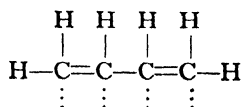
These structures call to mind the elaborate formulæ which used to be employed to represent double salts such as the alums. They differ profoundly from these however. The old formulæ for double salts were entirely speculative, if not indeed the useless products of idle hours. These formulæ for active principles, perfumes, alkaloids, and synthetic dyestuffs are the result of prolonged research and deep thought; and often their final form has been arrived at only after much controversy. They represent the products of molecular architecture built up atom by atom, as a master builder piles stone on stone to construct an edifice; and they are a monument alike to the complexity of nature and the genius of man.

Attention may next be drawn to some reactions of addition to unsaturated hydrocarbons, and a theory and method of formulation which have been put forward to explain them.

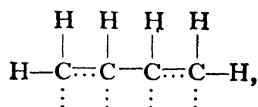
When 1 : 3 butadiene forms a dibromide the following reaction occurs:



Why, it may be asked, does the remaining double bond in the dibromide appear in a central position; why does not one double bond disappear without further change, with the formation of $\text{CH}_2\text{Br}-\text{CHBr}-\text{CH}=\text{CH}_2$? The answer probably is that the more symmetrical molecule is more stable. Then the further question arises by what mechanism the reaction which produces this molecule is effected. The answer is given by Thiele in his theory of "Partial Valencies".* According to this theory the affinities of the four carbon atoms in butadiene are not completely satisfied by the union into which these atoms have entered, so that to each carbon atom there is a free partial valency shown thus:



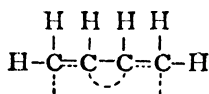
which is represented thus:



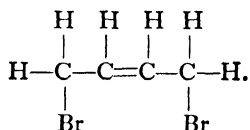
* *Ann.*, 1899, 306, 87.

94 SYMBOLS AND FORMULÆ IN CHEMISTRY

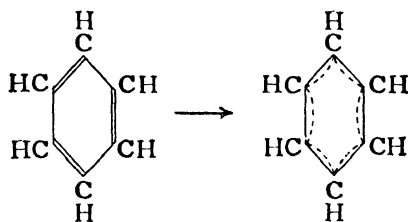
since no carbon atom can have a valency exceeding four. The partial valencies of the two inner carbon atoms are then supposed to approach and neutralize one another, so forming a "conjugated double bond", which may be represented thus:



Consequently, when the dibromide is formed, the bromine atoms attach themselves to the external carbon atoms where there are free partial valencies. The partial valencies between the carbon atoms then disappear, and the product becomes:

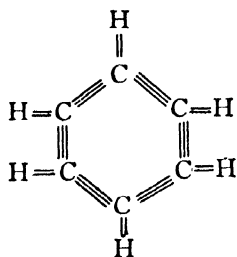


The theory finds many applications, an important one being to the benzene ring:



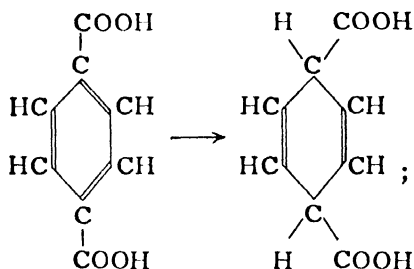
Thus by halving the three valencies represented by the double bonds and distributing the half-valencies round the ring, a symmetrical formula for benzene is obtained which makes the 1:2 and 1:6 positions equivalent, and renders Kekulé's dynamic hypothesis unnecessary.

It may be mentioned here, by anticipation, that the modern electronic theory of valency justifies the halving of the valency unit, since the completed shell of the carbon atom contains eight electrons, and in each ordinary bond two electrons participate. If, therefore, each electron is represented by a stroke, the formula for benzene becomes:

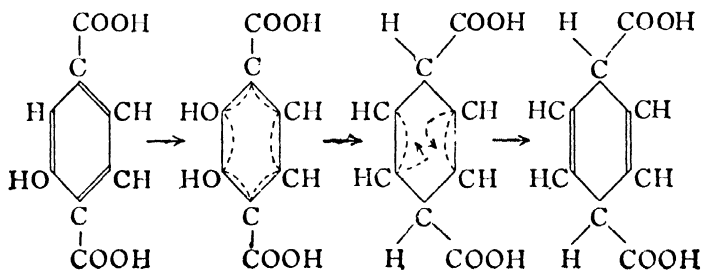


in which all the carbon atoms are similarly joined to one another and to the hydrogen atoms.

One further example of the use of Thiele's theory may be given. Terephthalic acid, when reduced yields Δ^{2-5} dihydroterephthalic acid thus:



in which the opening out of one double bond involves the moving of another in order to preserve symmetry. There is no difficulty in understanding this change on the partial valency theory. It is represented thus:



CHAPTER IV

The Development of Stereochemistry

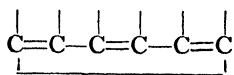
To find the beginnings of the idea of Stereochemistry, or "chemistry in space", with the corresponding use of stereochemical or tridimensional formulæ, it is necessary to go back to the year 1860. In January and February of that year Louis Pasteur delivered before the Chemical Society of Paris two lectures on "Asymmetry in Natural Organic Compounds", in which he gave an account of his discovery of the relation between racemic acid and dextro- and lævo-tartaric acids, and came to several conclusions, the first of which was this:

"When the atoms of organic compounds are asymmetrically arranged, the molecular asymmetry is betrayed by the crystalline form exhibiting non-superposable hemihedrisms."

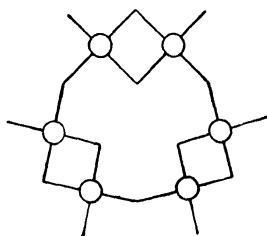
Applying this principle to the tartaric acids Pasteur asked and answered the following question: "Are the atoms of the dextro-acid grouped in the form of a right-handed spiral, or are they placed at the apex of an irregular tetrahedron, or are they disposed according to this or that asymmetric arrangement? We do not know."

In this sentence there is clearly a recognition of "chemistry in space", and a suggestion of a tetrahedral disposition of the atoms, though not of the valencies of carbon.

The next development seems to have come from Kekulé. In his *Chemie der Benzolderivate*, published in 1867, Kekulé interprets the benzene formula:



thus:



In this formula the valencies of the carbon atom are arranged

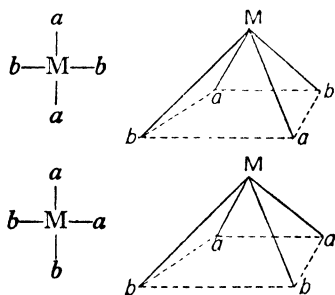
symmetrically at right angles to one another; they are not distorted to produce double bonds consisting of parallel lines. This figure is really the projection of a model of a benzene molecule, rather than a formula for benzene. The plane formula in common use takes no account of the directions in which the valency forces of the carbon atom act; it serves its purpose but is frankly conventional. When, however, the question of the direction in which the forces of valency act is raised, the way is opened for a quite new development in the structure theory. Can it be said that the valencies of the carbon atom are forces which extend from that atom in four directions at right angles, and all in the same plane? Crum Brown represented them so, and Hofmann constructed models to show them so. Kekulé, however, was a man of vision; he was an architect who was not content with plans, for he visualized models. So important is it to do justice to Kekulé's vision of the carbon atom, and the space-disposition of its valencies, that his own words on the subject may be quoted. Kekulé said (1867): "The four units of affinity of the carbon atom, instead of being placed in one plane, radiate from the sphere representing the atom in the direction of hexahedral axes, so that they end in the faces of a tetrahedron. . . . A model of this description permits of the union of 1, 2, and 3 units of affinity, and, it seems to me, does all that a model can do."

This, again, is chemistry in space; it is stereochemistry. Seven years after this time the development of stereochemistry was begun by Le Bel and van't Hoff. Yet it is clear that the genius of Kekulé first conceived the idea of the tetrahedral disposition of carbon valencies. What is wonderful is that the idea had not been thought of before. Dalton's atoms were spheres; what were his circular symbols but projections of spheres? Yet Dalton was content with projections, with shadows. Laurent thought of atoms arranged to form prisms and pyramids; yet no one through the intervening years asked for more than shadows. At length Pasteur required asymmetric molecules stretched through space; and then came Kekulé with carbon valencies stretched through space. "Let us dream," said Kekulé. The benzene ring was one dream of this master mind, the tetrahedral model of the carbon atom was another. Kekulé dreamed of the tetrahedral model; yet he had no use for it; the need and the use arose in quite another direction.

The conclusion of Pasteur that optical rotatory power is connected with molecular asymmetry, and the view of Kekulé that the four valencies of carbon radiate from the atom so as to "end in the

faces of a tetrahedron" contain the germ of the theory of "the asymmetric carbon atom". Yet this theory was not enunciated until the autumn of 1874, when J. A. Le Bel in Paris, and J. H. van't Hoff in Holland, put it forward simultaneously. Le Bel's thesis was "On the relations which exist between the atomic formulæ of organic bodies and the rotatory power of their solutions", whilst van't Hoff published his opinions in "A treatise on a system of atomic formulæ in three dimensions and on the relation between rotatory power and chemical constitution".

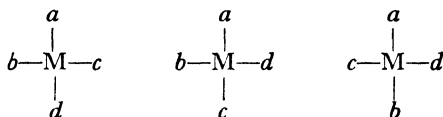
At the beginning of Chapter V of his *Arrangement of Atoms in Space** van't Hoff explains his fundamental conception that in the compound CR_4 there proceeds from the carbon atom an unknown force which tends to drive the groups united with carbon as far away from one another as possible, and that this brings the groups into a tetrahedral position. When the groups are identical, as in CH_4 , the tetrahedron is necessarily a regular one; but when otherwise there may be irregularity. Le Bel had more flexible ideas regarding the stereochemistry of carbon compounds; for, starting from the position of Pasteur, he developed the geometrical ideas of asymmetry, but did not emphasize the tetrahedral model. Consequently the ideas of van't Hoff, rather than those of Le Bel, are the foundation on which the stereochemistry of carbon compounds has been reared. The necessity for the tetrahedral model may be demonstrated by showing that another stereochemical formula, such as the square-pyramid formula, cannot be substituted for it. Indeed it may be seen that the square-pyramid formula is identical with the plane formula, so far as the representation of isomers is concerned. Thus both of these formulæ show two isomers of the type Ma_2b_2 ; viz.:



and the tetrahedral formula only one, which accords with experience;

* Longmans, 1898.

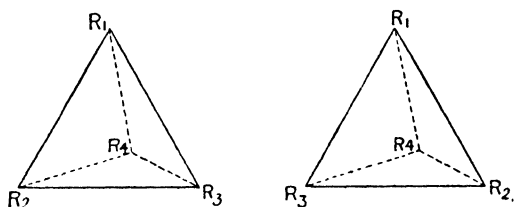
also both plane and square-pyramid formulæ show three isomers of the composition $Mabcd$, viz.:



but the tetrahedral formula only two, one of which is the mirror image of the other; which again is in accordance with experience.

Van't Hoff, indeed, pointed out that a plane formula predicted too many isomers of the type $CR_1R_2R_3R_4$. "So that," said van't Hoff, "to avoid having to account for such a large number of isomers there is only one supposition possible, namely that the four groups united to carbon occupy the angles of a regular tetrahedron at the centre of which the carbon atom itself is situated."

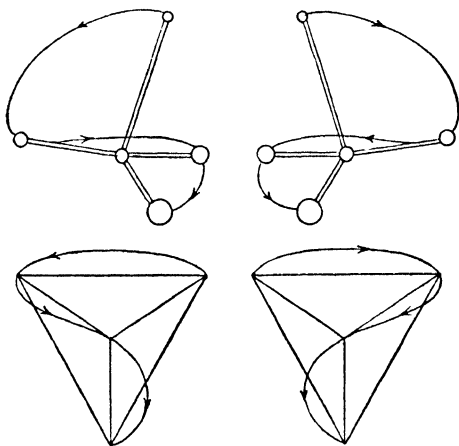
Van't Hoff then represented the two isomers having the formula $CR_1R_2R_3R_4$ thus:



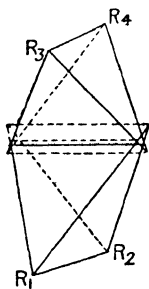
one formula being manifestly the mirror image of the other. By means of such formulæ he explained the activity of amyl alcohol $(CH_3)(C_2H_5)CH \cdot CH_2OH$, which contained four different groups attached to a central carbon atom, and the non-activity of citric acid $(CH_2CO_2H)_2COH \cdot CO_2H$, in which two of the four groups attached to a central carbon atom were alike. After exhaustive trial with different substituents the following generalization was reached: "Every carbon compound which in solution rotates the plane of polarised light contains an asymmetric carbon atom"; examples of such compounds being lactic, tartaric, and camphoric acids, and also the sugars. He further recognized that if, by substitution in a compound, asymmetry disappeared, optical activity disappeared with it; but that nevertheless a mixture in equal proportions of two oppositely active isomers would be inactive, a

phenomenon which came to be known as racemism, because it is the condition existing in the case of (inactive) racemic acid.

Werner in his *Lehrbuch der Stereochemie* (Jena, 1904), represents optical isomerism in the following way, which exhibits the object and image relation very plainly.



Van't Hoff went further, however, and applied his theory to "unsaturated bodies having two free atomicities". Thus he represented the double bond in ethylene and its derivatives by "two tetrahedrons having one of their edges common, so that the four groups R_1 , R_2 , R_3 , R_4 , combined respectively to the two atoms of carbon, occupy the free angles, and are situated in one plane". This mode of union was represented by the accompanying figure; and



it was pointed out that if R_1 differs from R_2 and R_3 similarly differs from R_4 , "there will be two different relative positions enabling us

to predict a case of isomerism not interpretable by the aid of the ordinary atomic formulæ"; that is to say, that if in the above figure R_1 and R_2 or R_3 and R_4 change places an isomer of the first compound is produced. Examples of such isomers were given by van't Hoff, including fumaric and maleic acids: $C_2H_2(COOH)_2$, but no attempt was made at this stage to say which was which.

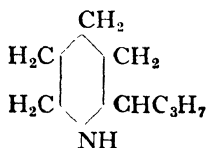
In May, 1875, van't Hoff published his pamphlet: *La Chimie dans l'Espace*, and in 1877 a German edition appeared entitled: *Die Lagerung der Atome im Raume*.

The new teaching was favourably received by Johannes Wislizenus, who found that it elucidated the problems concerning lactic acid on which he himself was engaged; but it was ironically criticized by Kolbe, now indeed a chemist of the old school, who, as Professor Sir James Walker says, "was tilting at graphic formulæ of every sort". *

Credit, indeed, must be given to Wislizenus for employing the idea of Chemistry in Space as early as 1869, because in this year he accounted for the optical activity of sarcolactic acid by the hypothesis of "different dispositions in space" of the constituent atoms of its molecule. The term geometrical isomerism was used by Wislizenus in 1873 for isomerism depending on the space-disposition of atoms in a molecule. The term "stereoisomerism" was first used by Victor Meyer in 1888.

In extending his theory, van't Hoff employed italics to show asymmetric carbon atoms in formulæ; e.g. tartaric acid, with two asymmetric carbon atoms was: $CO_2H \cdot CHOHC HOH \cdot CO_2H$. The starred symbol C^* has also been employed.

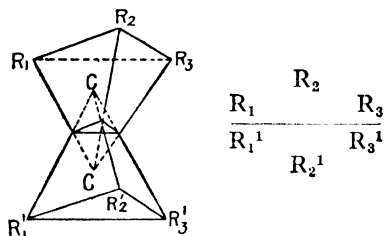
An asymmetric carbon atom, by an extension of the same principle, might also appear in the benzene nucleus, as, for example, in the case of coniine:



Instead of constructing tetrahedra for all stereochemical formulæ, which would be very troublesome, van't Hoff introduced "a very

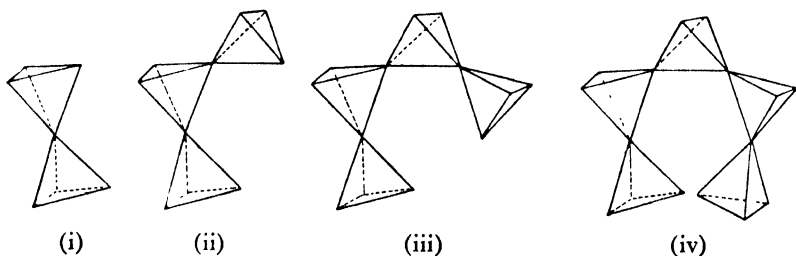
* *Vide* "Chemistry in Space" from van't Hoff's *Dix Années dans l'Histoire d'une Théorie*, translated by Marsh, 1891; also Walker's "van't Hoff Memorial Lecture," *J. Chem. Soc.*, 1913, 103, 1127.

simple notation by which the groups combined with the atoms of carbon are indicated". Thus the following formulæ are equivalent:



It is noteworthy that when the union of two carbon atoms by a single bond is to be represented by tetrahedra, the apices of these tetrahedra are here shown to penetrate one another to their respective centres, where the carbon atoms are supposed to reside, so that one valency unit of each carbon atom ends at the other carbon atom. This is evidently more correct than to represent the two tetrahedra as only touching one another at their apices, as is usually done, since in this case the linear distance between the two carbon atoms is twice as great as that between either carbon atom and another atom.

It may be pointed out here that when three or more singly linked carbon atoms form a chain, curvature of the system necessarily occurs if the forces of valency joining two carbon atoms together are represented as acting along the straight lines between the atoms. Now the angle between any two lines joining the centre of a regular tetrahedron with its corners is equal to $109^\circ 28'$. This then is the angle between two adjacent sides of neighbouring tetrahedra in the accompanying figures, and it is seen that five but not six of such



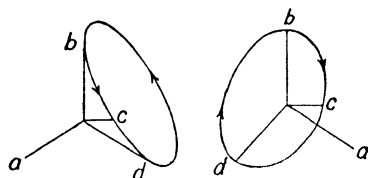
tetrahedra can be accommodated without overlapping; for the angle between the sides of a regular pentagon is 108° , whilst that between the sides of a regular hexagon is 120° . Thus the difference

between $5 \times (109^\circ 28')$ and $5 \times 108^\circ = 6^\circ 40'$ accounts for the small gap shown in fig. (iv) below. Further reference will be made to these facts when v. Baeyer's strain theory is considered.

In order to present the salient features of the stereoisomerism of carbon in as brief a form as possible, it will be well to consider the application of the theory to the following kinds of carbon linkage: (a) single-bond linkage, (b) double-bond linkage, (c) linkage in the benzene ring, (d) triple-bond linkage.

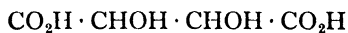
(a) *Stereoisomerism of carbon compounds with single-bond linkage.*

—The simplest case is that of compounds of the type $\text{CR}_1\text{R}_2\text{R}_3\text{R}_4$, i.e. compounds containing one asymmetric carbon atom. The molecules of such compounds are of two kinds, which are related to one another as object and image, and rotate the plane of polarized light equally to right and left respectively. This relationship has already been illustrated by Werner's method on p. 100; the accompanying figures also show the opposite rotations in the two isomers in orbits which include the letters *b*, *c*, *d*, in the same order. Crystals



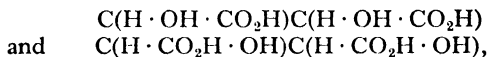
of such compounds are hemihedral, and similarly of two kinds, i.e. they exist in right- and left-handed forms; so that both molecules and crystals are said to be enantiomorphously related (Gr. *ἐναντίος* = opposite). It was this kind of isomerism which was first studied by Le Bel and van't Hoff.

Examples of compounds containing two asymmetric carbon atoms united by a single bond are furnished by the tartaric acids, including racemic acid. It was the "resolution" of sodium ammonium racemate into the dextro- and laevo-tartrates which constituted the great achievement of Pasteur; and concerning the stereochemical explanation of observed phenomena van't Hoff claimed that "the theory receives its most complete verification from the isomerism of the tartaric acids:

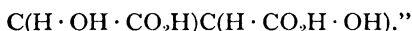


There are known two isomers with equal and opposite rotatory

powers, represented, according to the above demonstration, by the following symbols:



together with their inactive combination, racemic acid, which has been mesotomized by Pasteur. But the special feature of the case is the existence of an inactive amesotomic isomer, also discovered by Pasteur . . . and representable by the following formula:



These relationships are seen better by the actual stereochemical formulæ, built according to van't Hoff's own model:

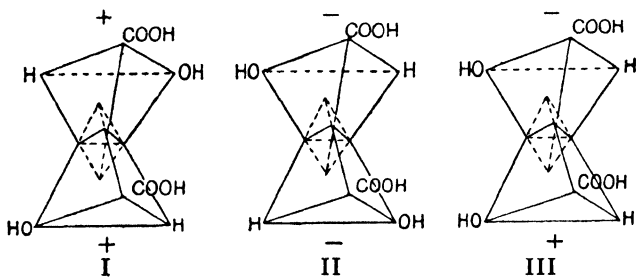
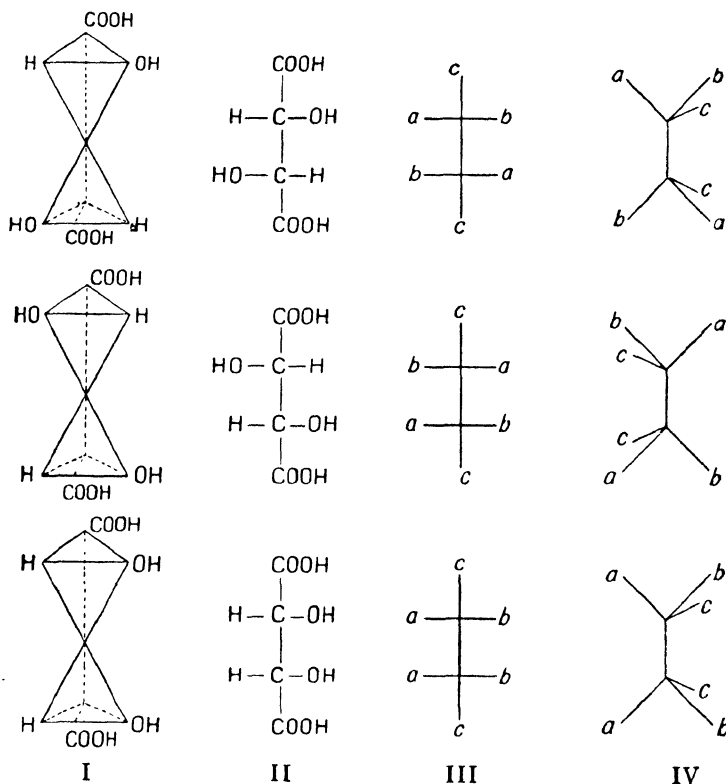


Fig. I represents dextro-, fig. II lævo-, and fig. III meso-tartaric acid. The two tetrahedra of I are identical, and, if separated, superposable; the H and OH appear on opposite sides in the two parts only because one tetrahedron is inverted relatively to the other. The same remark applies to II, but II is the mirror image of I, i.e. enantiomorphous in relation to it. Therefore if I represents dextro-tartaric acid, II must represent the lævo-acid to which it is equal and opposite in every respect. I can be externally compensated by II, and if these two are mixed in equal proportions there results racemic acid, which, being composed of two optical antipodes in equimolecular proportions, is optically inactive, but resolvable into the antipodal molecules which exist together in it. The choice of these formulæ is, however, arbitrary to the extent that the actual disposition of the groups on the tetrahedra is unknown; that is to say, formula II might just as well represent the dextro-acid, and formula I the lævo. Fig. III represents meso-tartaric acid because it shows internal compensation; that is to say, the half of the for-

mula above a horizontal plane at right angles to the paper is the mirror image of the half below it. Thus meso-tartaric acid is incapable of resolution into optical antipodes; it cannot be "meso-tomised", in the language of van't Hoff.

The connexion between steric (I) and plane (II) formulæ is clearly seen when the steric formulæ are represented in projection thus:



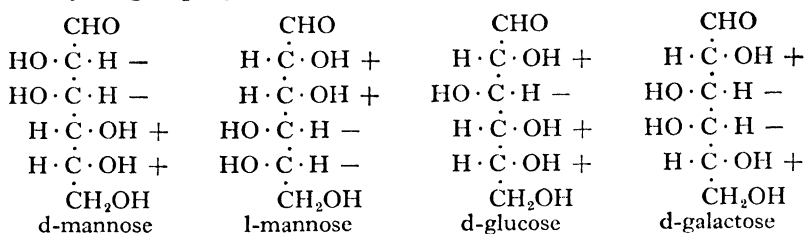
E. Fischer, however,* has abbreviated these formulæ, for general purposes, so that they take the form shown in III.

A slightly different way of representing the same facts, which suggests the framework of tetrahedra, is shown in IV.

Prec-eminent among optically active compounds containing singly-bound carbon atoms are the various sugars, whose constitution has been elucidated by E. Fischer and others. It will suffice to give a

* *Ber.*, 1891, 24, 2684.

few aldohexoses, having the empirical constitution $C_6H_{12}O_6$, with four asymmetric carbon atoms, and possessing five alcoholic and one aldehydic grouping:

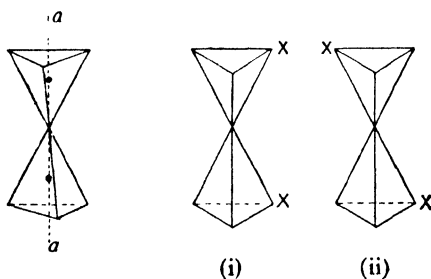


According to the Geneva nomenclature these sugars have the generic name hexanepentolal. Moreover, Fischer has made a suggestion, which again is arbitrary, but convenient, that, starting from the aldehydic group, the grouping $H \cdot \dot{C} \cdot OH$ should be regarded as + and $HO \cdot \dot{C} \cdot H$ as -. These signs are placed after the formulæ and are seen to correspond with the signs attached to the tetrahedral formulæ for the tartaric acids given above.

It is to be observed that all these sugars are optically active, since none of them shows a plane of symmetry with corresponding internal compensation. This is because, although in three out of the four cases the + and - signs compensate one another on either side of the centre of the formula, one end of each molecule is aldehydic and the other alcoholic.

(b) *Stereoisomerism of carbon compounds with double-bond linkage.*

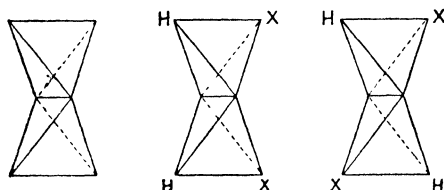
Consider a compound containing the grouping $\begin{array}{c} \diagup \\ C \\ \diagdown \end{array} - \begin{array}{c} \diagdown \\ C \\ \diagup \end{array}$. Let this be represented by two tetrahedra joined at their apices, and on a common axis $a \dots a$.



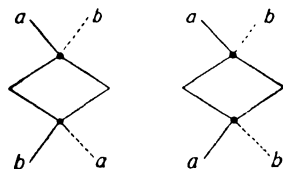
Let the compound be a derivative of ethane C_2H_6 , in which one

hydrogen atom attached to each carbon atom has been replaced by the group X. Then it appears from the figure that, if the two tetrahedra upon their common axis are immovable relatively to one another, two stereoisomeric compounds $C_2H_4X_2$ will exist. If, on the contrary, one of these tetrahedra, with its attachments, can rotate relatively to the other until form (i) is converted into form (ii), or vice versa, such isomerism will be destroyed. The fact is that no isomerism of $C_2H_4X_2$ derivatives exists; consequently the two tetrahedra must be supposed to be, not fixed, but free to rotate on their common axis until the most stable configuration is reached.

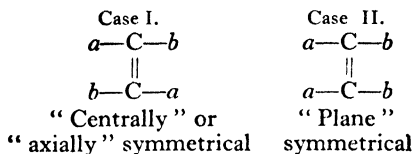
Now consider unsaturated compounds containing the grouping $\times C=C \times$, say ethylene derivatives of the type $C_2H_2X_2$. Le Bel and van't Hoff represented the stereochemical formula for ethylene and its derivatives by two tetrahedra united along a common edge, or with edges interpenetrating; and since there is now no question of rotation about a point, and rotation about a common edge seems impossible, the formula suggests two isomers, as the following figures show:



Thus compounds of the type $Cab : Cab$ can be represented as existing in two forms, which may be formulated thus:



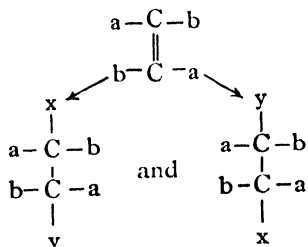
or



Consider the two cases separately.

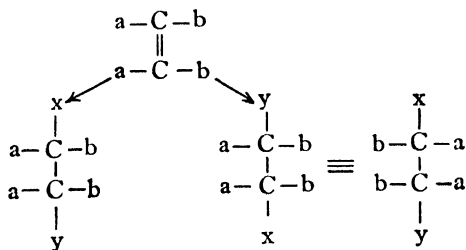
Case I.—Let the elements of xy be added to the compound $C_2a_2b_2$ in the two ways shown in the following diagram, the same bond being ruptured in each case to provide free valencies for the attachment of x and y .

The products are identical, for it can be seen that one is the inverted form of the other. This is shown convincingly by constructing the formulæ with the usual models, balls of different colours being used to represent



a , b , x , and y . Now let x and y be added in the same relative positions, but with the rupture of different bonds in the two cases. Two formulæ are obtained, as may be made clear by models, one of which is the mirror image of—i.e. enantiomorphous with—the other; and this is the case irrespective of the relative positions taken up by x and y in the two formulæ.

Case II.—Let the elements of xy be added in relatively opposite positions in two cases, and with the rupture of the same double bond; two enantiomorphous formulæ will then be produced thus:



If, however, x and y are made to take different relative positions in two molecules, and at the same time different bonds are ruptured in the process, the two products are identical because the one difference of change neutralizes the other. Now it is apparent that the

formula $x-\overset{\overset{a}{\cdot}}{\underset{\underset{b}{\cdot}}{C}}-\overset{\overset{b}{\cdot}}{\underset{\underset{a}{\cdot}}{C}}-y$ or $y-\overset{\overset{a}{\cdot}}{\underset{\underset{b}{\cdot}}{C}}-\overset{\overset{b}{\cdot}}{\underset{\underset{a}{\cdot}}{C}}-x$ (Case I) contains two asym-

metric carbon atoms, and the compound which it represents must be optically active. Such a compound, however, is not produced in chemical synthesis, for asymmetric molecules are never formed without an equivalent formation of their optical antipodes, so that

a racemic and inactive mixture results. If, therefore, xy is added

to the molecule $\begin{array}{c} a \quad b \\ \dot{C}=\dot{C} \\ b \quad a \end{array}$, one or other of the constituent bonds of the

double bond being ruptured in the process, it must be supposed that the compound suffers change in these two ways in equimolecular proportions. This, indeed, is to be expected, for the two constituent parts of the double bond are equal, and there is no reason why this bond should suffer disruption in one way more than in the other. The product is thus the same enantiomorphous mixture

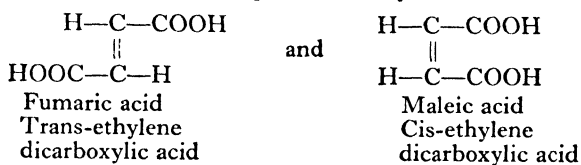
as results when xy is added to $\begin{array}{c} a \quad b \\ \dot{C}=\dot{C} \\ \dot{a} \quad \dot{b} \end{array}$ (Case II).

Indeed, as was pointed out by W. H. Perkin, Junr.,* whenever, in general, the unsaturated group $a-C-b$ is converted into the

saturated one $\begin{array}{c} x \\ a-\dot{C}-b \\ | \\ -C- \\ | \\ y \end{array}$ right-handed and left-handed, i.e. enantio-

morphously related individuals are produced in equivalent amounts, so that a racemic mixture rather than an optically active compound results.

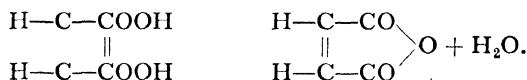
This kind of isomerism was studied by Wislizenus; and the simplest case of it is presented by fumaric and maleic acids, $C_2H_2(COOH)_2$, which are represented by the formulæ:



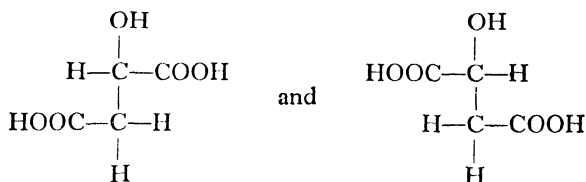
The prefixes *trans*- and *cis*-, used to describe these two forms, are self-explanatory (*trans* across, *cis* on this side). It may be asked, however, how it is decided which formula to apply to one acid and which to the other. The answer is that maleic acid, when heated alone or with dehydrating agents, easily forms an anhydride, whilst no anhydride of fumaric exists; for doubtless the loss of the elements

* Wislizenus Memorial Lecture, *J. Chem. Soc.*, 1905, 87, 524.

of water by two carboxyl groups will depend upon their juxtaposition, so that the following reaction may occur:

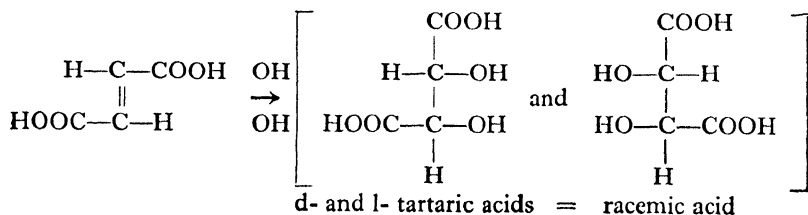


To illustrate the transformations studied above, the combination of these acids with the elements of water, H and OH representing x and y , may first be considered. The product is malic acid, $\text{C}_2\text{H}_3(\text{OH})(\text{COOH})_2$, an acid which contains an asymmetric carbon atom, and can therefore exist in the enantiomorphously related forms:

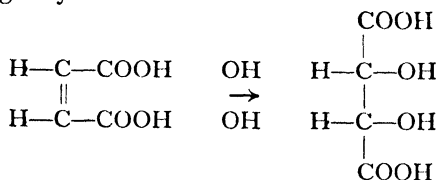


Thus three forms of malic acid exist: a dextro-rotatory form, a lævo-rotatory form, and an inactive ($d + l$) form; l -malic acid exists in apples and other fruits, and the ($d + l$) acid is formed synthetically. According to the theory developed above ($d + l$) malic acid should result from the addition of the elements of water to either fumaric or maleic acid, for it has been concluded that the addition of xy to $\text{C}_2a_2b_2$ must always produce a mixture in equimolecular proportions of the d and l modifications of the type $\text{C}_2a_2b_2xy$. Inactive malic acid is actually formed in this way from either fumaric or maleic acid; and thus theory and experience are in accord.

A second change which fumaric and maleic acids can undergo, however, is oxidation, by which an OH group is added to each carbon atom. Fumaric acid then suffers disruption of one or other constituent of the double bond, and the result is the mixture of d - and l -tartaric acids which constitutes racemic acid. Thus:



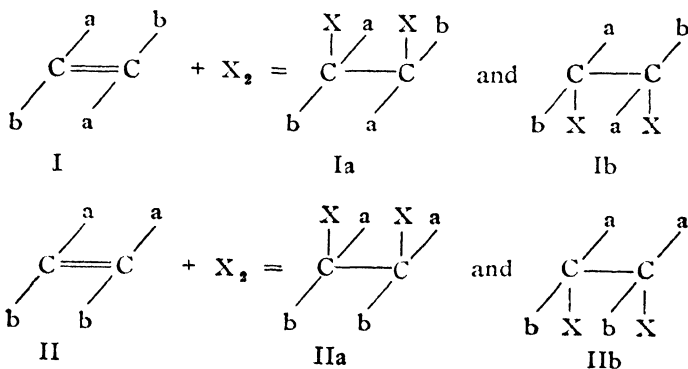
Regarding the oxidation of maleic acid, a simple change represented in the following way:



in which two OH groups are introduced by the disruption of the double bond, results in the formation of inactive, internally compensated, meso-tartaric acid.

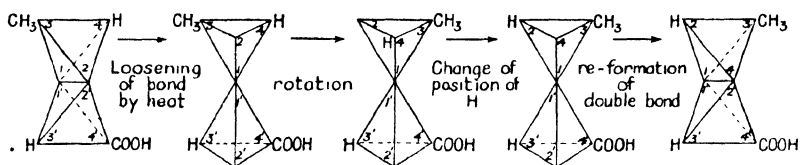
If different members of the pair of bonds were to suffer disruption in equal numbers throughout the reacting quantity of maleic acid, racemic acid would result, as in the case of fumaric acid. Since, however, this does not occur, we learn that whilst the molecules of carbon compounds, uninfluenced by the life of an organism, tend to a condition of symmetry, this condition is reached in the simplest way, which in this case is the way of internal rather than external compensation.

Another way of formulating changes like the above is to represent the third dimension by slanting bonds. Thus in the formulæ that follow *a* and *b* are supposed to lie with the C-atoms in the plane of the paper, and XX' to be situated either above or below that plane. Consequently the reaction $\text{C}_2\text{a}_2\text{b}_2 + \text{X}_2 = \text{C}_2\text{a}_2\text{b}_2\text{X}_2$ is thus represented:

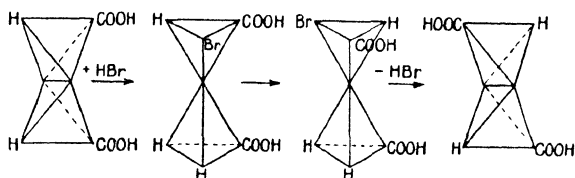


Ia and *Ib* are the formulæ of optical antipodes, e.g. d- and l-tartaric acids. *IIa* and *IIb* represent identical intramolecular inactive forms, e.g. mesotartaric acid.

Certain transformations of compounds of this kind which are brought about by heat may now be noticed, because stereochemical theory gives an account of them. Thus crotonic and isocrotonic acids are respectively the *cis*- and *trans*- varieties of methyl-ethylene-carboxylic acid, $C_2H_2CH_3 \cdot COOH$. The conversion of isocrotonic into crotonic acid at 180° is represented in the following way, since it is believed to be made possible by the temporary loosening of the double bond. The reaction proceeds in this direction rather than the other because the CH_3 group has a greater affinity for the negative $COOH$ group than has hydrogen. It involves, however, the migration of a hydrogen atom from one position to another, as the figures show:

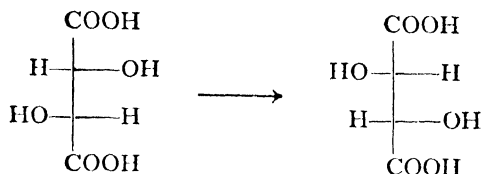


The transformation of maleic into fumaric acid by hydrogen bromide involves the addition of the elements of HBr , through the rupture of the double bond, and their subsequent removal, after the rotation of one half of the resulting molecule of monobromsuccinic acid into a more stable position relative to the other half:

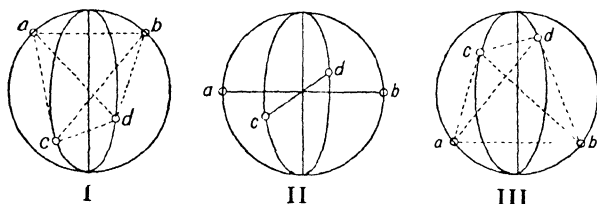


Similar to these phenomena are those of racemisation, i.e. the conversion of 50 per cent of an optically active compound into its optical antipode, so that the product is inactive because it consists of the dextro- and lævo-varieties in equal amounts. Thus when dextro-tartaric acid is heated for some time with water at 175° it is converted into racemic acid, i.e. the inactive mixture of dextro- and lævo-tartaric acids; and when dextro-phenylbromoacetic acid is kept in benzene solution at atmospheric temperature it very slowly becomes inactive. Such a spontaneous change is called autoracemisation.

Now for half of the molecules of dextro-tartaric acid to undergo the change:



it appears necessary for two of the three groups, say H and OH, in each half of the molecule to change places. No doubt the water and high temperature employed promote lability, and make possible the change which is necessary for equilibrium. Werner,* however, has devised a model to show how this change may take place without the actual splitting off of atoms from the molecule:

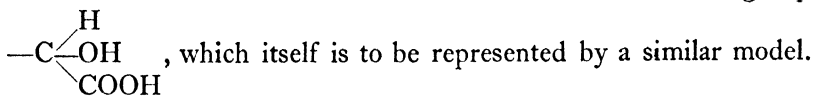


The figures show a sphere intersected by two planes at right angles. The carbon atom is at the centre of the sphere, and the groups represented by the small balls *a*, *b*, *c*, *d*, are so situated on the surface of the sphere that the lines joining them form a regular tetrahedron, as is shown by the dotted lines in I. It is now supposed that the balls are free to vibrate in either direction around the circle on which they are situated so that they may come to the positions shown in II. When, however, all the four balls reach the central plane at the same instant there is no reason why any of them should proceed into one hemisphere rather than the other. Procedure to the condition shown in III, in which each ball has migrated into the opposite hemisphere, is therefore just as likely to occur as reversion to the condition shown in I. III, however, is the mirror image of I, as may be seen by inverting it; and a mixture in equal proportions of molecules in the conditions shown by these two figures is a racemic mixture in which two optical antipodes have neutralized one another.

Thus racemization is accounted for; it is nevertheless rather difficult to apply this explanation to the case of the tartaric acids,

* *Lehrbuch der Stereochemie.*

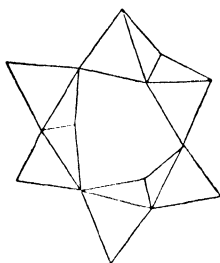
for one of the balls in the above models must stand for the group



(c) *Stereoisomerism of carbon compounds containing the benzene ring.*

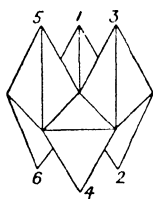
—When Kekulé's well-known benzene formula  is expressed

stereochemically by means of tetrahedra joined alternately at points and edges, it takes the form illustrated in the figure.* This figure shows all the free angular points of the tetrahedra, and therefore

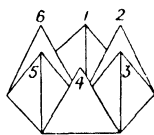


Stereochemical form of Kekulé's
Benzene Formula

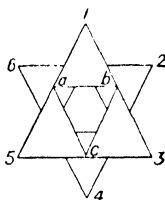
all the hydrogen atoms, to lie in one plane. It is acceptable just so far as the plane formula of Kekulé is acceptable; but alternative formulæ have been proposed, which are as follows:



Formula of
Marsh and Vaubel



Formula of v. Baeyer,
Marsh, and Loschmidt

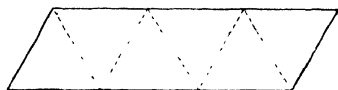


Formula of
Sachse

The formula of Vaubel differs from that of v. Baeyer by showing the H atoms of benzene in two planes, atoms at positions 2, 4, 6 being in a plane parallel to that containing atoms at positions 1, 3, 5; whereas in v. Baeyer's formula all the H atoms are in one plane. The formula of Sachse is constructed by erecting regular tetrahedra

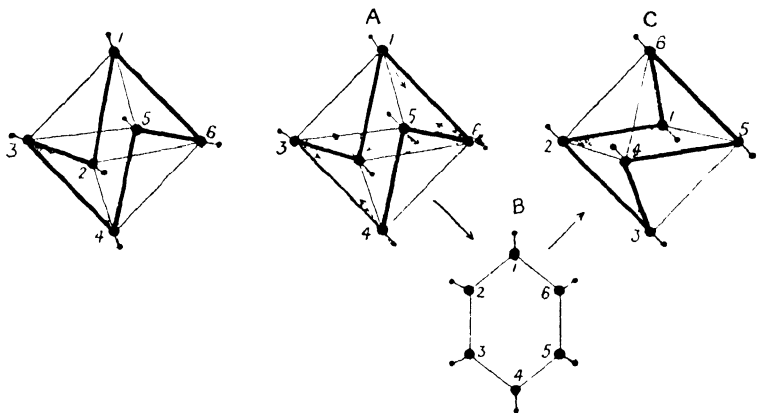
* *Vide Graebe, Ber., 1902, 35, 526.*

on six of the eight faces of a regular octahedron, a pair of faces which are parallel being omitted. The small triangle *abc* in the figure is the outline of one of the missing faces of the octahedron, and within it are seen parts of the outline of the other missing face. A model of such an octahedron may be made by cutting a piece of cardboard into the shape shown below, bending it along the dotted lines, and fastening the ends together.



Regarding the merits of these different models, Graebe* is of opinion that the first of them is preferable to the others; although it is subject to the same defect as Kekulé's benzene ring, since it makes the relation 1 : 6 to differ from the relation 1 : 2. The chief reason for this preference is that unless all the C and H atoms lie in one plane asymmetry with ortho- and meta-di-derivatives arises.

A notable space-formula for benzene is that of Collie.† In this formula the six carbon atoms are supposed to be situated at the



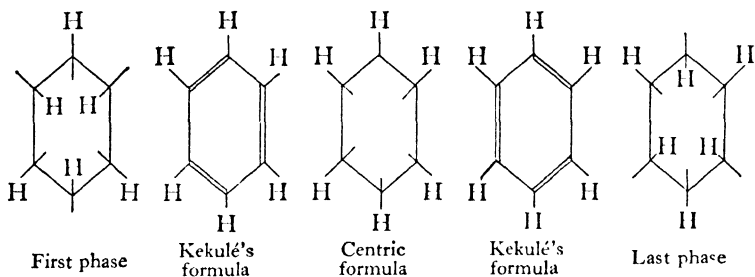
angular points of a regular octahedron—or, what is the same thing, the centres of the six edges of a regular tetrahedron, or of the six faces of a cube, and united by bonds—shown in the figure by thick lines—so that each carbon atom is united to two others. The carbon atoms are supposed to be free to vibrate about the centre of gravity of the molecule in such a manner that from one extreme position

* *Loc. cit.*

† *J. Chem. Soc.*, 1897, 71, 1013; 1916, 109, 561.

they pass through a plane into another extreme position. These positions are shown in figs. A, B, C.

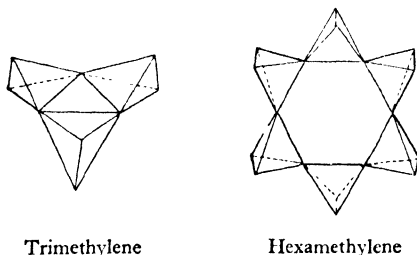
In passing through these three phases the molecule assumes configurations, the plane projections of which correspond with the Kekulé formula in its two positions, as well as with the centric formula, thus:



There are, moreover, seen to be two sets of hydrogen atoms, the 1, 3, 5 set, and the 2, 4, 6 set.

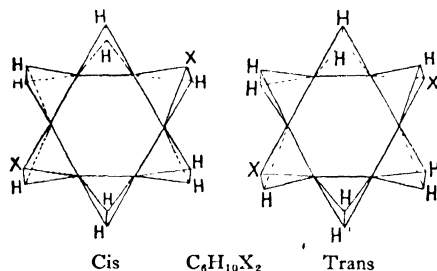
It is claimed for this space-formula not only that it most accurately accounts for the reactions and derivatives of benzene, but also that it accords with the space-lattice of the solid hydrocarbon.

Polymethylenes and their Derivatives.—The polymethylenes, $(CH_2)_n$, where $n = 3$ to 6 or more, are cyclic hydrocarbons, containing no double bond. The most important of these are trimethylene, C_3H_6 , and hexamethylene or hexahydrobenzene, C_6H_{12} . Such compounds are represented stereochemically by tetrahedra joined at their apices to form closed systems, as for example:

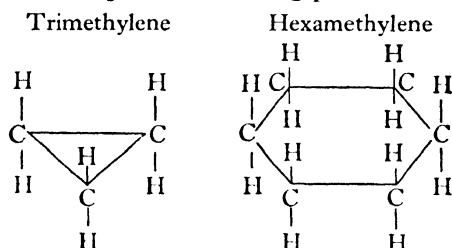


Now in these systems there are three parallel planes containing respectively n H-atoms, the n C-atoms, and the remaining n H-atoms, the distance between the H-planes being represented by the length of side of a tetrahedron. Consequently with di-derivatives, such as those of hexamethylene, $C_6H_{10}X_2$, there should be two stereo-

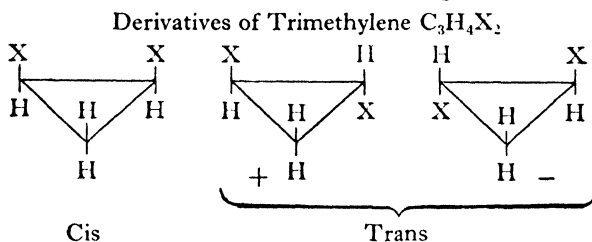
isomers, in one of which both the X-groups lie in one plane (cis-form) and in the other in different planes (trans-form). These are shown in the following figures, in which the X's are related to one another in the para-position:



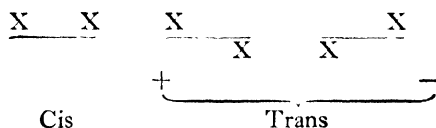
Instead of drawing tetrahedra to represent these stereochemical formulæ van't Hoff adopts the following plan:



and the formulæ can be made additionally clear by the omission of the C-symbols, cis- and trans-derivatives being shown thus:



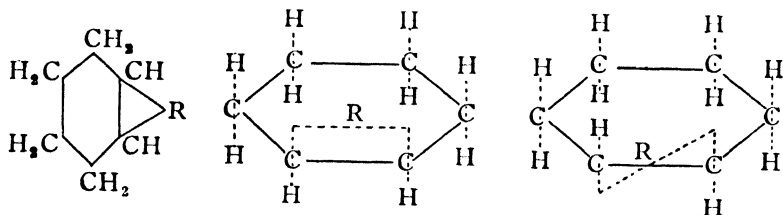
A still simpler way of indicating these isomerides has been adopted by Aschan*, viz.:



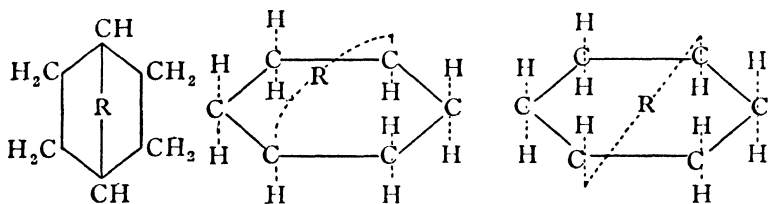
* *Ber.*, 1902, 35, 3389.

It thus appears that two enantiomorphous forms of the trans-derivative are possible, and some optically active compounds of this kind have actually been obtained.

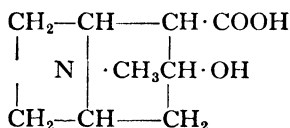
When two carbon atoms in the hexamethylene ring are linked by means of a bivalent radical R, cis- and trans-modifications can exist, and are indicated in the following ways:



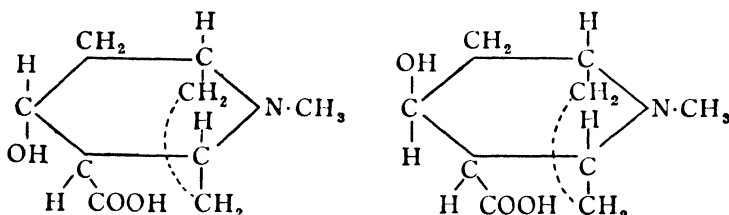
and



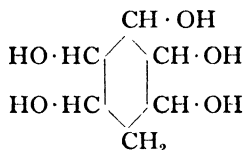
An actual example of stereoisomerism allied to that of the hexamethylene derivatives is furnished by the ecgonines or tropine-carboxylic acids, whose constitution is shown by a plane formula to be:



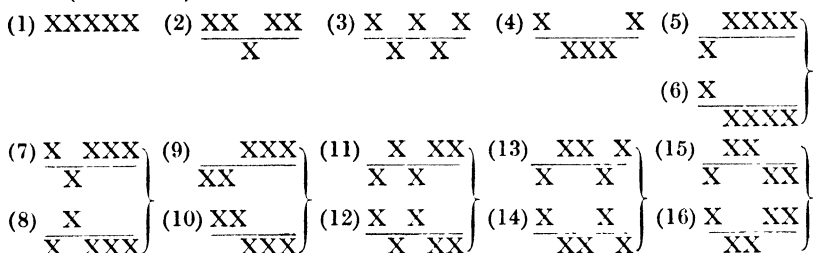
The two modifications of this compound, which differ in their physiological action, are represented stereochemically, thus:



With some hexamethylene derivatives a large number of stereoisomers are possible. For instance, quercitol or pentahydroxy-hexamethylene



is theoretically capable of existing in four inactive, and six pairs of active forms, which are represented according to Aschan's method * thus (X = OH):



This is a convenient place to give a brief account of v. Baeyer's *Strain or Tension Theory*; since this theory was framed to account for the relative stabilities of the polymethylenes. The theory† was expressed in the following words:

"The four valencies of a carbon atom act parallel to lines joining the three corners of a regular tetrahedron with its centre, making an angle of $109^{\circ}28'$ with one another. The directions of the valencies can be altered, but such alteration produces a strain whose amount is proportional to the angle through which the valencies are diverted."

Now when carbon atoms unite to form a ring the bonds which join the atoms together in one plane are supposed to form a regular polygon; in the case of trimethylene an equilateral triangle, of tetramethylene a square, and so on. Thus the deviation of each bond from its normal position is equal to half the difference between $109^{\circ}28'$ and the angle between any two sides of the polygon.

These angles of deviation are calculated to be as follows:

	Angle of Deviation.
Ethylene (Dimethylene) = $\frac{1}{2}(109^{\circ}28' - 0^{\circ}) =$	$54^{\circ}44'$
Trimethylene = $\frac{1}{2}(109^{\circ}28' - 60^{\circ}) =$	$24^{\circ}44'$
Tetramethylene = $\frac{1}{2}(109^{\circ}28' - 90^{\circ}) =$	$9^{\circ}44'$
Pentamethylene = $\frac{1}{2}(109^{\circ}28' - 108^{\circ}) =$	$0^{\circ}44'$
Hexamethylene = $\frac{1}{2}(109^{\circ}28' - 120^{\circ}) =$	$-5^{\circ}16'$
Heptamethylene = $\frac{1}{2}(109^{\circ}28' - 128^{\circ}34') =$	$-9^{\circ}33'$
Octamethylene = $\frac{1}{2}(109^{\circ}28' - 135^{\circ}) =$	$-12^{\circ}46'$

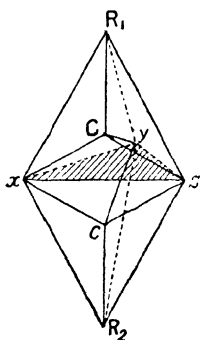
* *Loc. cit.*

† *Ber.*, 1875, 18, 2277.

It thus appears that in the formation of pentamethylene the carbon valencies undergo the least deviation, and therefore that of all the polymethylenes this compound should be the most stable; also that hexamethylene comes next in stability, and that tetramethylene and heptamethylene should be about equally stable. These conclusions are borne out by experience as regards compounds with positive deviation, but do not apply to the higher polymethylenes where the deviations are negative.

(d) *Stereoisomerism of carbon compounds with triple bond linkage.*—

The stereochemical formulæ of carbon compounds having a single bond between two carbon atoms are expressed by tetrahedra joined through their apices, and the corresponding formula representing a double bond by two tetrahedra joined along their edges; consequently the more intimate contact implied by a triple bond is expressed by two tetrahedra lying face to face, the bonds being supposed united through the angular points of the triangular surface. Thus the compound $R_1 \cdot C \equiv C \cdot R_2$ is represented stereochemically by the accompanying figure which takes the form of a double three-sided pyramid, the triangular surface common to both pyramids being the shaded portion, xyz . All that need be said about such a structure, as regards isomerism, is that this does not occur. R_1 may be the same as R_2 as in acetylene, or different, as in its derivatives; but R_1 and R_2 cannot be differently related to the carbon atoms, for if they change places this only inverts the figure, it does not affect the molecule which the figure represents.

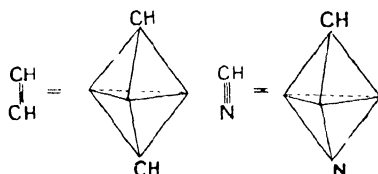


The Stereochemistry of Nitrogen.—By the stereochemistry of nitrogen is meant the stereochemistry of compounds which depends on the space-disposition of the valencies of the nitrogen atoms they contain. Compounds of trivalent and quinquivalent nitrogen have to be considered; and these are principally the oximes and diazo-compounds, and the substituted ammonium derivatives.

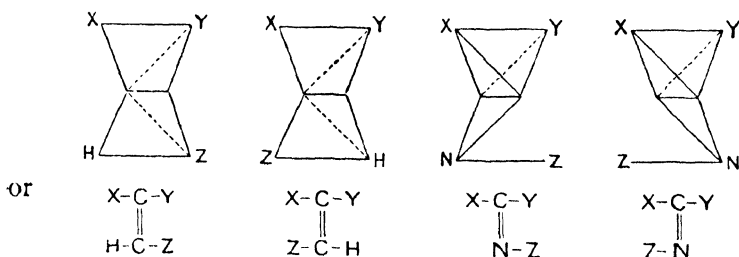
The Hantzsch-Werner hypothesis to account for the isomerism of the oximes and diazo-compounds is as follows*: "The three valencies of the nitrogen atom in certain compounds are directed towards the angles of a (not necessarily regular) tetrahedron, in whose fourth angle the nitrogen atom itself is situated."

* *Ber.*, 1890, 23, 11.

Regarding this hypothesis there are two remarks to be made. The first is that the valencies of the N-atom do not lie in a plane, but are inclined together on one side of it. The condition may be realized by supposing that three rods are hinged loosely to a sphere representing the N-atom so as at first to lie in a plane with its equator, and that the sphere is then lifted above the plane whilst the rods fall away so as to have their ends resting on the plane after the manner of a tripod. The second remark is that nothing is said here about the disposition of the valencies of the nitrogen when that atom is uncombined; the special dispositions of the various atoms, including the N-atom, being considered as the result of forces acting between them within the molecule which contains the N-atom. In discussing the theory Hantzsch* compares (N) with (CH), e.g. in the two compounds $\text{HC} \equiv \text{CH}$ and $\text{HC} \equiv \text{N}$, in which there can be no stereoisomerism, as the following figures show:

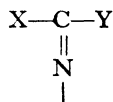


He then shows that compounds of the type $\text{XYC} = (\text{N})\text{Z}$, as, for example, the oximes, where $\text{Z} = \text{OH}$, are analogous to ethylene derivatives of the type $\text{XYC} = (\text{CH})\text{Z}$. Consequently the stereochemistry of the oximes is compared with that of compounds of the fumaric and maleic acid types, as the following formulæ show:



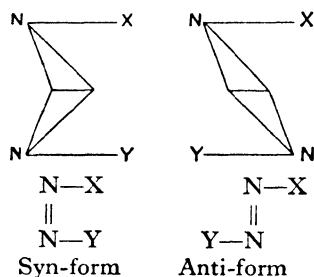
It is worth while to point out here that if the three valencies of the N-atom had been symmetrically disposed in one plane, i.e. with an angle of 120° between them, a double bond formed by two valencies drawing together would be in a straight line with the

remaining valency, so that the configuration would take the following form, and there would be no stereoisomerism:



It might be supposed, however, that when X differed from Y the atom or group attached to the spare N-valency would be attracted in the direction of either X or Y; but this would not give two forms.

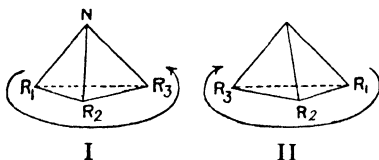
Hantzsch next compares diazo-bodies of the type $\text{XN}=\text{NY}$ with ethylene derivatives of the form $\text{X}(\text{CH})=(\text{CH})\text{Y}$, and consequently develops two stereochemical formulæ thus:



Finally, he shows that if the valencies of nitrogen do not lie in the same plane as the atom, stereoisomerism should occur with

compounds of the type $\text{N} \begin{smallmatrix} \nearrow \text{R}_1 \\ \nearrow \text{R}_2 \\ \searrow \text{R}_3 \end{smallmatrix}$, which is analogous to $\text{CH} \begin{smallmatrix} \nearrow \text{R}_1 \\ \nearrow \text{R}_2 \\ \searrow \text{R}_3 \end{smallmatrix}$.

Thus the two following formulæ are enantiomorphous; for if II is turned over so as to bring R_1 and R_3 into the same positions as in I,



R_2 will be above the plane of the paper in one case and below it in the other. Substituted hydrazines would be a special case of such isomerism, enantiomorphous forms corresponding with the formulæ $\text{X}-\text{N}-\text{Y}$ and $\text{X}-\text{N}-\text{Y}$ being suggested. No such isomers

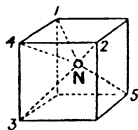


containing trivalent nitrogen exist, however; so that the separate

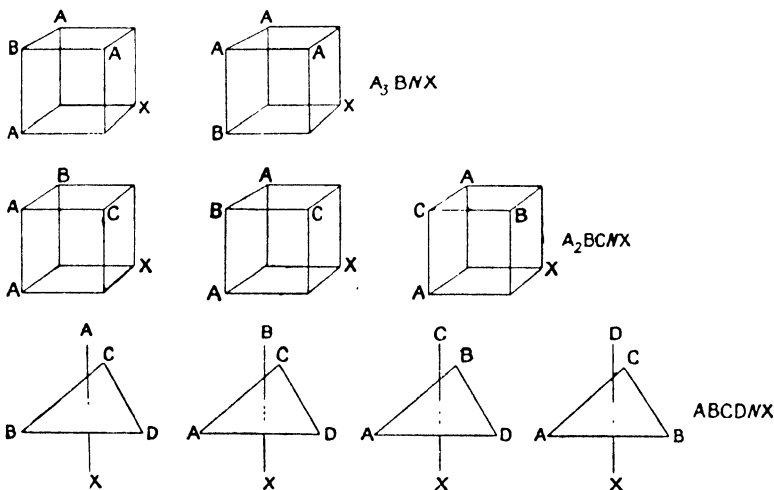
valencies of nitrogen in ammonia and its derivatives seem to lie in one plane; and the Hantzsch-Werner hypothesis does not apply to these compounds.

Substituted ammonium derivatives of the type $ABCDNX$ can, nevertheless, exist in enantiomorphous forms. This was first shown by Le Bel* who resolved methyl-ethyl-propyl-isobutyl-ammonium, chloride into optically active components. Various configurations have been proposed to show the space-disposition of the five radicals or atoms around the N-atom.

The first of these is the cube of van't Hoff:



The N-atom is represented in the centre of the cube, the points 1, 2, 3 corresponding with the positions of the radicals A, B, C, whilst D is at 4 and X at 5, 4 and 5 being at the ends of a diagonal. The following isomers appear possible according to this model:

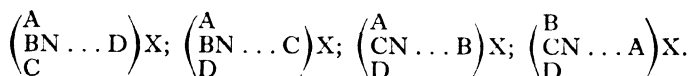
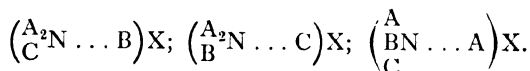
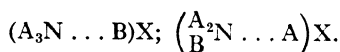


In the four figures representing possible isomers of the type $ABCDNX$ the triangle, as stated above, is formed by joining the points 1, 2, 3 of the cube, and the vertical axis by joining points 4 and 5.

Next may be noticed the formulæ of Werner which are part of this chemist's theory of valency (q.v.).

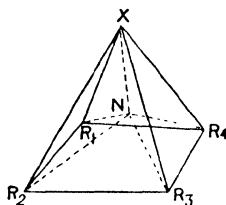
* *Compt. rend.*, 1891, **112**, 724.

Werner formulates ammonium salts thus: $\text{H}_3\text{N} \dots \text{HX}$, which he expresses graphically thus: $\left(\begin{array}{ccc} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{N} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array} \right) \text{X}$, the broken line representing a secondary valency. Now if the valency unit represented by the broken line differs from the other three units the following isomers are possible in the case of substituted ammonium salts:

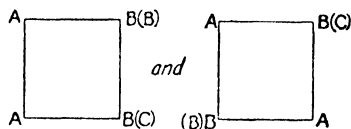


Werner's formula gives the same number of isomers in each case as the cubical formula of van't Hoff.

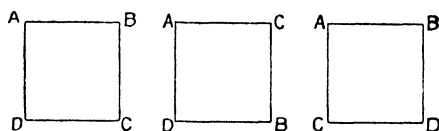
Lastly there is the square-pyramid formula of Bischoff and



Wedekind. It shows no isomerism of compounds of the type $(\text{A}_3\text{N} \cdot \text{B})\text{X}$; two configurations for $(\text{N} \cdot \text{A}_2\text{B}_2)\text{X}$ and $(\text{NA}_2\text{BC})\text{X}$:



and three configurations for $(\text{NABCD})\text{X}$:



These formulæ are alike in showing more isomers than exist

in the case of substituted ammonium derivatives. They show this because the quinquivalency of nitrogen is represented as requiring five atoms or groups to be attached to the central N-atom. According to the modern view, however, ammonium salts, whether simple or substituted, are regarded as completely ionized under all circumstances, so that their stereochemistry is to be accounted for by representing four and not five atoms or groups disposed round the N-atom. In other words, it is the stereochemistry of the ion $(\text{NH}_4)^+$, or $(\text{NR}_4)^+$, which alone has to be considered; and the problem therefore becomes identical with that of the stereochemistry of carbon compounds of the type (CR_4) . Such compounds show stereoisomerism, with optical activity, only when all four groups attached to the carbon atoms are different. That, moreover, is the only kind of isomerism which has been detected with substituted ammonium derivatives; so that the special space formulæ given above disappear because the familiar tetrahedron serves for all purposes.

The stereochemistry of other elements.—The interesting stereochemical phenomena presented by carbon and nitrogen compounds, and particularly those of enantiomorphism and optical activity, stimulated research to discover similar phenomena regarding compounds of other elements. The field was a large one, for there were many polyvalent elements whose atoms might become the nuclei of compounds manifesting asymmetry with accompanying optical activity. For example, silicon is related to carbon and phosphorus to nitrogen; what then about the stereochemistry of silicon and of phosphorus? So successful have been the researches in this field that, in addition to those of carbon and nitrogen, optically active derivatives of the following seventeen elements have been produced*:

Boron.

Silicon, tin.

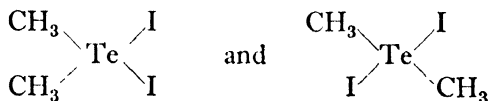
Phosphorus, arsenic.

Sulphur, selenium.

Chromium, iron, cobalt, rhodium, iridium, platinum.

Beryllium, zinc, copper.

Tellurium, also, has been shown to form two stereoisomeric forms of dimethyltellurium di-iodide:



* Vide Lowry, *Chemistry and Industry*, 1927, 78, 102.

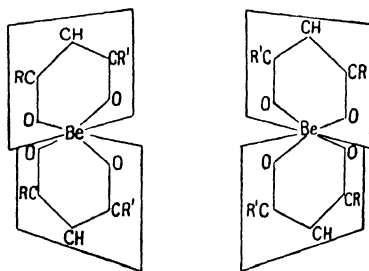
which must be represented as having a square configuration, unlike that of methylene iodide to which they are otherwise analogous in type.

Active sulphonium derivatives maintain their activity when ionized in water, so that the ion $\left[\begin{array}{c} R_1 \\ \diagdown \\ S-R_3 \\ \diagup \\ R_2 \end{array} \right]^+$ is asymmetric.

In this it differs from substituted ammonias $\left[\begin{array}{c} R_1 \\ \diagdown \\ N-R_3 \\ \diagup \\ R_2 \end{array} \right]$, and it is therefore concluded that the three radicals in the sulphonium ion do not lie in the same plane with the sulphur atom.

The stereochemistry of the seven elements beginning with chromium is of a different kind. It is connected with the formation of amines and allied compounds by these elements, and is referred to an octahedral configuration around the central atom. This kind of isomerism is embraced by Werner's theory which will shortly be dealt with.

It is remarkable that beryllium zinc and copper atoms, which are normally bivalent, can become centres of optical activity; and this fact has been represented by formulæ * in which the beryllium or other atom is shown co-ordinated with four oxygen atoms, which are disposed tetrahedrally about it. So two optical antipodes containing beryllium are represented by the following formulæ which are related as object and image:



* Mills and Gotts, *J. Chem. Soc.*, 1926, 3121.

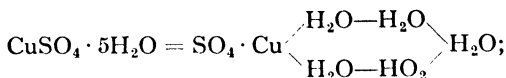
CHAPTER V

Special Theories of Valency

I. *Werner's Co-ordination Theory*.—No one can read a textbook of inorganic chemistry without discovering a large and varied array of compounds whose constitution cannot be expressed by graphic formulæ with bonds employed as these are employed in organic chemistry. It is not necessary to go beyond the formulæ of the commonest hydrated salts to discover the difficulty of representing constitution. Consider, for example, crystallized copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It has been usual to express CuSO_4 graphically

thus: $\text{Cu} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{S} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array}$, without regard to the crystal water. Yet since

this water changes the colour of the copper sulphate from white to blue, it is certain that it occupies an important place in the constitution of the salt. And since the colour of an aqueous solution of copper sulphate, which contains cupric ions, resembles the colour of the crystallized salt, it may be inferred that water is intimately associated with the cupric ion in the case both of the solid salt and its solution. This simple illustration shows the need of extending the theory of the constitution of inorganic compounds. It is true that chain or ring formulæ have been invented for crystallo-hydrates (Wurtz) by assuming oxygen to be quadrivalent, and for ammines (Blomstrand) by making nitrogen quinquivalent, thus:



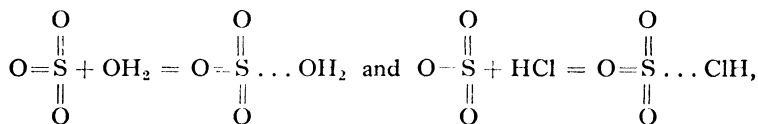
but such formulæ have no evidence to support them, and do not, therefore, appear to be justified.

It is well to recognize at once that whilst there are in inorganic chemistry numerous binary compounds—"compounds of the first

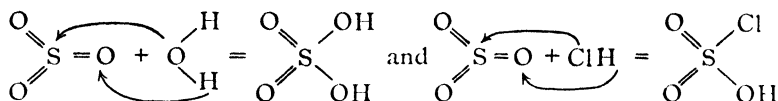
order"—whose constitution can be accounted for by the rigid application of the usual ideas of valency; there are also many other compounds—"complex compounds or compounds of a higher order"—which cannot be so accounted for.

In view of this fact Werner proposes first to hold rigid views of valency in abeyance, and to consider compounds of a higher order from another point of view, viz. that of "co-ordination". By co-ordination is meant the arrangement and attachment of a number of atoms or groups in space round a central atom; the co-ordination number being the number of atoms or groups so arranged and attached. And inasmuch as other valencies will be called into play in the formation of such compounds, there may be recognized two orders of valency: principal valencies and secondary or auxiliary valencies (Haupt- und Neben-Valenzen).

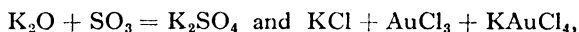
Werner * introduces his theory by assuming that OH_2 and HCl can become attached to SO_3 by secondary valencies, thus:



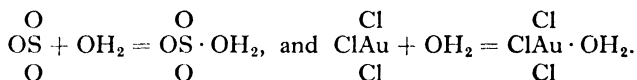
because the more electronegative O and Cl are attracted to the more electropositive S, the usual way of representing such combinations, viz.:



being regarded as incorrect. He then suggests an analogy between the following two reactions:



and justifies this analogy by showing that AuCl_3 , like SO_3 , can combine with OH_2 , thus:



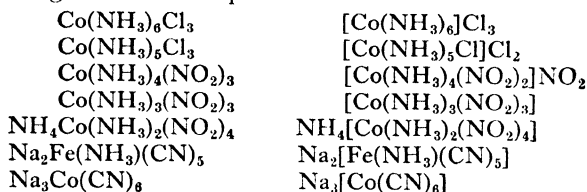
Compared with the rigid conception of bonds, these ideas seemed vague and unsatisfactory, and were received with scepticism.† Yet

* *Neure Anschauungen auf dem Gebiete der anorganischen Chemie*; or, English edition, *New Ideas on Inorganic Chemistry*, translated by E. P. Hedley, Longmans, 1911.

† *Vide*, e.g. Stewart's *Stereochemistry*, 1919, p. 158.

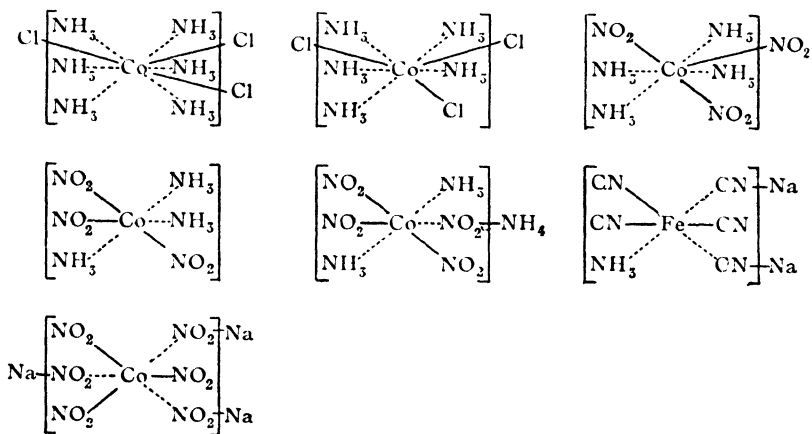
it will appear when the electronic theory of valency is reviewed in a later portion of this book, that they are in harmony with, and, indeed, a remarkable forecast of that theory.

Probably the best known compounds which serve to exemplify Werner's theory are the cobaltammines and allied bodies. Consider the following series of compounds:



In the first column are given the empirical formulæ of a series of seven compounds in which the numbers of ammonia molecules present continuously diminish from 6 to 0; and in the second column the complex radicals present in these compounds, as shown by electric conductivity and in other ways, are indicated by means of square brackets. Thus in the second compound the loss of a molecule of ammonia is compensated by the chlorine atom which ceases to be an acidic ion and enters the basic complex. In this way the valency of the complex group containing the cobalt atom falls throughout the series from +3 to -3; i.e. it undergoes a change from the state of a trivalent basic radical through a non-valent neutral state to the state of a trivalent acidic radical.

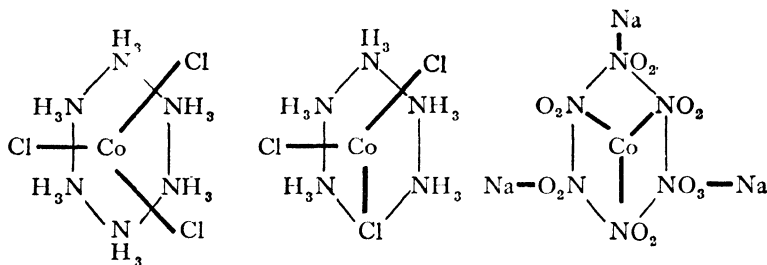
To account for such a series of compounds Werner postulates principal and auxiliary valencies, which are shown in the following formulæ as continuous and broken lines respectively:



The normal valency of the cobalt or iron atom in these six compounds is 3. Hence the following rule:

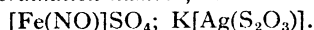
The combining power of the basic radical present in ammine and allied compounds is always found to be equal to the difference between the normal valency of the metal, and the number of acidic radicals included within the complex group containing the metal.

For example, in the ferric compound $\text{Na}_2[\text{Fe}(\text{NH}_3)(\text{CN})_5]$ the valency is $3 - 5 = -2$; i.e. the complex group is a dibasic acidic radical, as its sodium salt shows. Other examples are shown by $\text{K}^+[\text{AuCl}_4]^-$, $\text{K}^{++}[\text{PtCl}_6]^{--}$, &c. J. N. Friend,* however, postulates the existence of free and latent valencies, which he represents by thick and thin lines respectively; he also supposes that in ammines and similar compounds a shell of ammonia or other molecules surrounds the central atom. He therefore constructs formulæ for, say, the first, second, and seventh of these compounds in the following way:

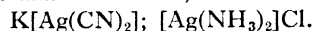


Reverting to Werner's formulæ, it is seen that six atoms, radicals or molecules are associated with the nuclear atom in the formulæ hitherto given. Thus the *co-ordination number* in these compounds is six; but this number may range in different classes of compound from 1 to 8, as the following few examples show:

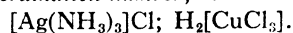
Co-ordination number, 1:



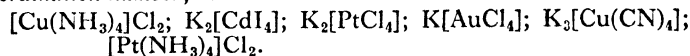
Co-ordination number, 2:



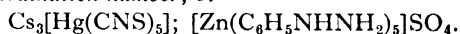
Co-ordination number, 3:



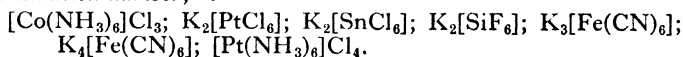
Co-ordination number, 4:



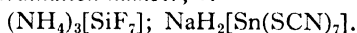
Co-ordination number, 5:



Co-ordination number, 6:



Co-ordination number, 7:



Co-ordination number, 8:

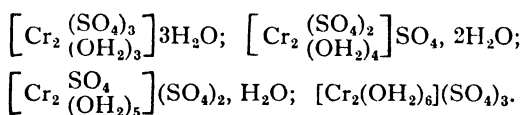


These examples show the wide sweep of Werner's theory, and method of formulation. The following examples of compounds formulated in the ordinary way, and according to Werner's method, serve further to illustrate the theory:

Usual Formula.	Werner's Formula.
$\text{Cr}_2(\text{SO}_4)_3, 6\text{H}_2\text{O}$	$[\text{Cr}_2(\text{OH}_2)_6](\text{SO}_4)_3.$
$\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}.$	$[\text{Cr}(\text{O}_2\text{H}_4)_6] \begin{smallmatrix} \text{SO}_4 \\ \text{SO}_4\text{K}. \end{smallmatrix}$
$\text{K}_2\text{SO}_4, \text{CuSO}_4, 6\text{H}_2\text{O}.$	$[\text{Cu}(\text{OH}_2)_6](\text{SO}_4\text{K})_2.$
$\text{K}_2\text{PtO}_3, 3\text{H}_2\text{O}.$	$\text{K}_2[\text{Pt}(\text{OH})_6].$
$\text{FeCl}_3, 6\text{H}_2\text{O}.$	$[\text{Fe}(\text{OH}_2)_6]\text{Cl}_3.$
$\text{NH}_4\text{Cl}.$	$[\text{NH}_4]\text{Cl}.$

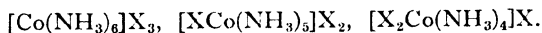
The inclusion of water of crystallization within the basic complex in some of these formulæ seems justified by the fact that H_2O can take the place of NH_3 in amines; but to write the formula $\text{K}_2\text{PtO}_3, 3\text{H}_2\text{O}$ as $\text{K}_2[\text{Pt}(\text{OH})_6]$ so as to resemble $\text{K}_2[\text{PtCl}_6]$ seems more open to question.

Werner's method of formulation is further illustrated by the following formulæ for varieties of hexahydrated chromic sulphate; which show, co-ordinated with chromium, non-ionized sulphate as part of the basic complex in lieu of water molecules, and in the last formula, where sulphate is completely ionized, a hexahydrated chromic ion: $[\text{Cr}_2(\text{OH}_2)_6]$, as present in the violet sulphate whether solid or in solution. Moreover, attention may be drawn to Werner's method of writing water as (OH_2) when it is co-ordinated in the basic complex:

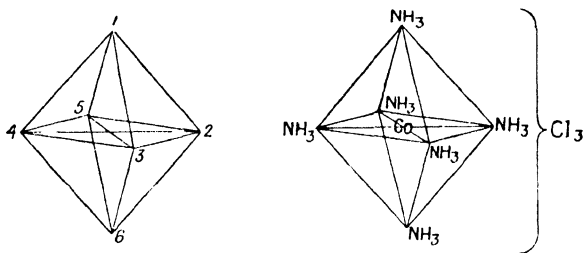


Thus far Werner's theory has served to account for the constitutions of a large number of diverse chemical compounds by means

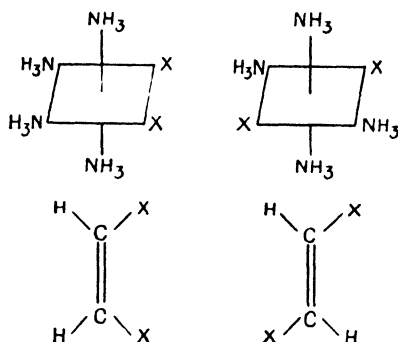
of plane formulæ without recourse to stereochemical conceptions. Among the cobaltamines, however, there are cases of isomerism which Werner found it necessary to account for by means of stereochemical models. Thus consider the series:



The first two of these compounds exist in only one form; but two forms of the third compound are known, which are green and violet, and are called praseo- and violeo-cobaltamines respectively. The first prepared compounds of this kind contained NO_2 groups, and it seemed possible that the isomerism might be connected with the NO_2 group; but Werner subsequently found that salts of the composition $[\text{Cl}_2\text{Co}(\text{NH}_3)_4]\text{X}$ exhibited the same phenomenon. Thus his stereochemical formulæ have been justified. What the configuration of such a formula should be it is easy to understand; for just as the most symmetrical figure representing the disposition in space of the four valencies of, say, the carbon atom is the regular tetrahedron, so the most symmetrical figure to represent the space-disposition of the six atoms or groups around the cobalt atom in cobaltamines is the regular octahedron, in the centre of which the cobalt atom is situated. This is shown in the following figures, the second of which represents hexammine cobaltic chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$:

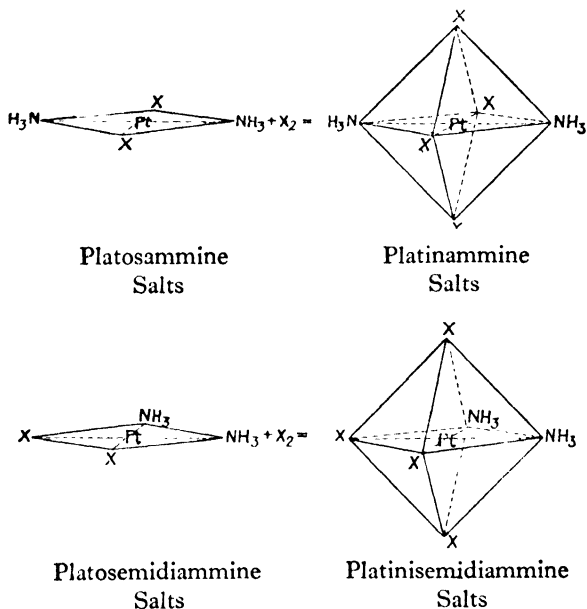


It has been found unnecessary in practice, however, to construct the whole octahedron, as the following formulæ show. Now it is apparent that the pairs of positions 1-2 and 1-6 in the octahedron are different; for 1-2 is a cis- and 1-6 a trans-position. Only two pairs are possible, however; for positions 2-3 and 2-4 for example, are the same relatively as positions 1-2 and 1-6. Werner draws attention to the analogy between this cis-trans isomerism and that of ethylene derivatives in the following way:

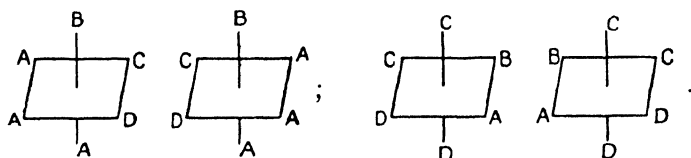


A remarkable case of isomerism exists, moreover, in the case of platinum amines; for there are two neutral platinumous compounds of the type $[\text{X}_2\text{Pt}(\text{NH}_3)_2]$, and these by the addition of X_2 produce two corresponding platonic isomers $[\text{X}_4\text{Pt}(\text{NH}_3)_2]$.

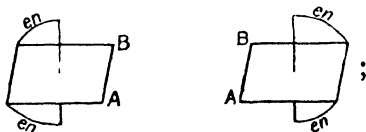
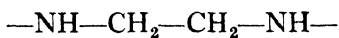
The former of these compounds corresponds in type to methylene chloride CH_2Cl_2 , which, however, exists in only one form because the four atoms are disposed round the carbon atom tetrahedrally. If these atoms had been disposed in one plane there would have been two isomers; therefore plane formulæ are adopted for the platinumous, and octahedral formulæ for the platonic isomers, thus:



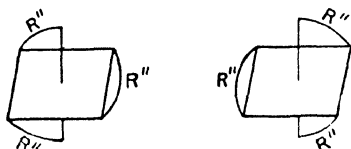
With such stereochemical formulæ as these a further question arises: that of asymmetry and optical isomerism. To produce asymmetry it is not necessary that all six groups surrounding the central atom should be different; thus it is shown below that octahedral complexes of the type XA_3BCD or $XABC_2D_2$ contain no plane of symmetry, and therefore can exist in two forms which are related to one another as object and image, and are optically active:



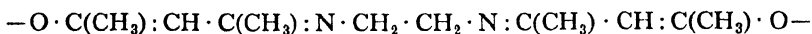
The optical activity thus suggested has been realized by Werner with compounds of chromium and cobalt containing ethylenediamine residues *en* =



and also with salts of the ferrous tri- α -dipyridyl radical $[\text{FeDipyr}_3]^{+}$, which can be formulated thus:



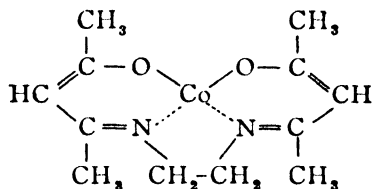
R'' may also be the oxalato-group $(\text{C}_2\text{O}_4)''$, as well as other bivalent radicals, including tetramminodihydroxycobaltic bromide $(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Br}$, which is a cobaltic ammine minus two NH_3 molecules. Such compound radicals, which are capable of occupying and holding firmly two positions in a co-ordinated complex have been called by G. T. Morgan chelate groups, from "chela", the great claw of the lobster.* It has also been shown that three and even four co-ordination positions may be occupied by a single radical behaving like a four-pronged fork. Such radicals or groups are called tri- and quadri-dentate groups. Thus two molecular proportions of $\alpha\beta\gamma$ -triaminopropane can occupy the six co-ordination positions round cobalt or rhodium atoms, forming the complexations $[\text{Cotp}_2]'''$ and $[\text{Rhtp}_2]'''$ † and a single molecular proportion of ethylene diaminobisacetylacetone, i.e.



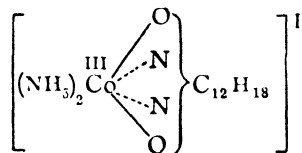
* *J. Chem. Soc.*, 1920, **117**, 1457.

† Pope and Mann, *Proc. Roy. Soc.*, 1925, **107**, 80.

has been shown by Morgan to occupy four co-ordination positions. The following formula shows how this is possible*:



the broken lines indicating the attachment of the N-atoms to the Co-atom by residual affinity, just as the N of NH_3 is attached in a simple ammine. The remaining two co-ordination positions are occupied by NH_3 molecules, not shown in the above formula, and since the whole complex is a univalent cation its constitution is represented briefly thus:



The stereochemical possibilities of such a complex are interesting. They depend upon what corners of the octahedron are occupied by the two NH_3 molecules, leaving four corners for the quadridentate group. Morgan and Smith represent these possibilities by the following formulæ:

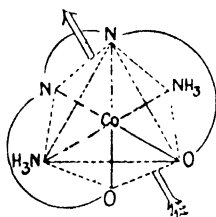


Diagram I

Two Planes of Symmetry intersecting in One Dyad Axis of Symmetry.

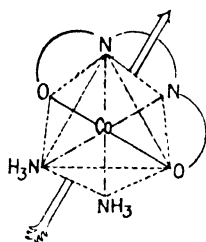
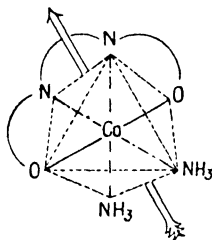


Diagram II

Cis-trans Enantiomorphous Pair each with One Dyad Axis of Symmetry and small optical activity.

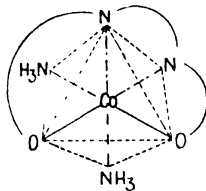
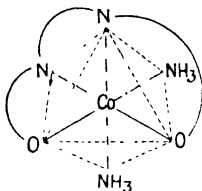


Diagram III

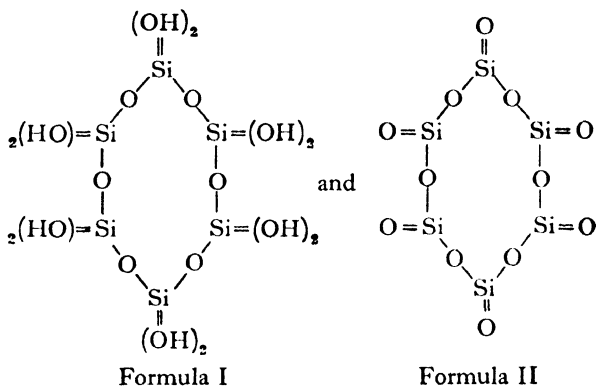
Cis-cis Enantiomorphous Pair without elements of Symmetry and with high optical activity

* Morgan and Smith, *J. Chem. Soc.*, 1925, 127, 2030.

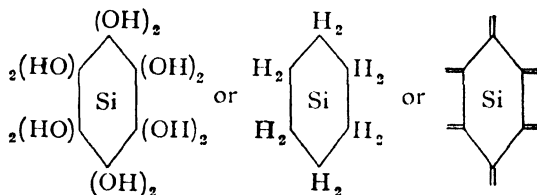
Attention may be drawn in these figures to the mode of representing the edges of the octahedron by dotted lines (. . . .), the principal valencies of the cobalt atom by continuous lines, the auxiliary valencies by broken lines (- - - - -), the dentate unions by curved lines, and the axis of symmetry by an arrow.

II. *The Hexite-Pentite Theory of W. and D. Asch.**—The study of the natural silicates, and the problems of their constitution, have engaged the attention of both mineralogists and chemists. Accepting the view that the natural aluminous silicates are salts of complex alumino-silicic acids, W. and D. Asch develop the theory that these minerals are closed rings consisting of 6- or 5-fold polymers of hydrated or anhydrous SiO_2 and Al_2O_3 , which are represented symbolically thus:

Silica.



Formula I is then abbreviated thus:

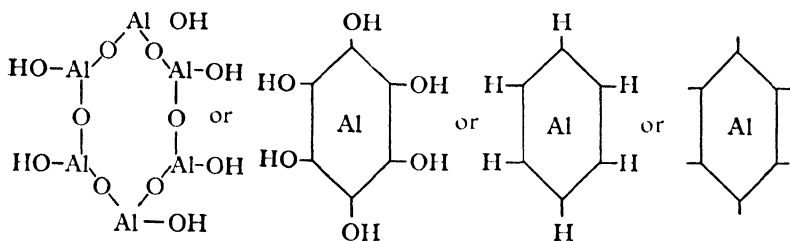


and formula II for $(\text{SiO}_2)_6$ likewise receives the simplified formula,

$\boxed{\text{Si}}$ which represents "silicon hexite".

* *Vide The Silicates in Chemistry and Commerce*, by W. and D. Asch, translated by Alfred B. Searle, Constable & Co., 1913.

Alumina.—Hydrated alumina, or aluminic acid, is:

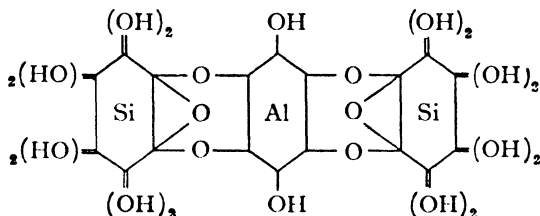


 representing $3\text{Al}_2\text{O}_3$, or aluminium-hexite.

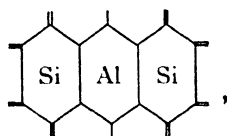
The symbols for the two hexites are then abbreviated further to $\hat{\text{Si}}$ and $\hat{\text{Al}}$; whilst the corresponding symbols for the pentites are

 and , and in their shortest form $\overline{\text{Si}}$ and $\overline{\text{Al}}$.

These authors then proceed to use silicon and aluminium hexites and pentites as the building stones or nuclei of the complex aluminosilicic acids and their anhydrides. Thus from one aluminium hydrohexite, and two silicon hydrohexites, i.e. from $3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $2(6\text{SiO}_2 \cdot 6\text{H}_2\text{O})$ is derived the formula:



which is abbreviated to

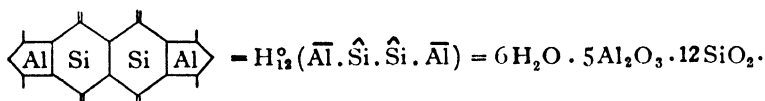
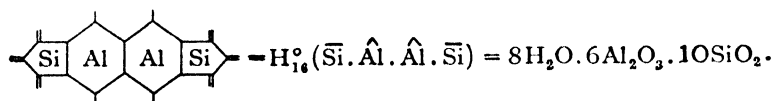


and finally to $\text{H}_{18}^{\circ}(\hat{\text{Si}} \cdot \hat{\text{Al}} \cdot \hat{\text{Si}})$.

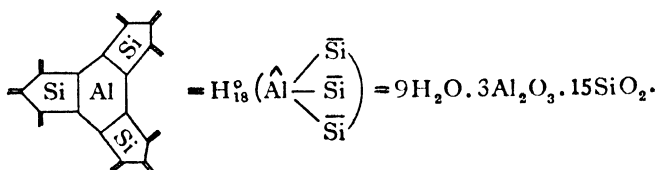
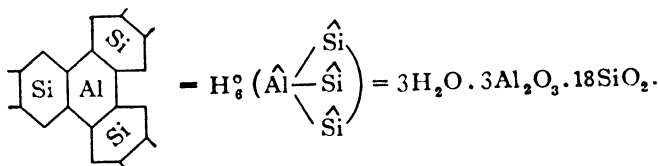
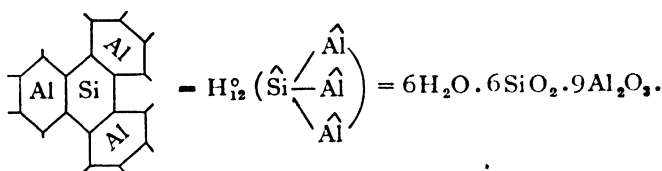
The expression H_{18}° shows that there are 18 HO groups in the graphic formula, derived from $9\text{H}_2\text{O}$ in combination with anhydrous SiO_2 or Al_2O_3 .

Silicon or aluminium pentites may also occur in combination; but an even number of the latter must always be present because one

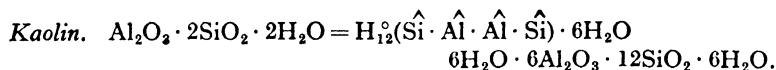
aluminium pentite represents $\frac{1}{2}(\text{Al}_2\text{O}_3)$. The following formulæ contain pentites:



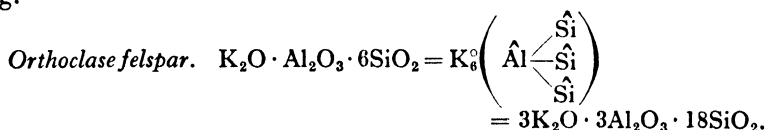
A silicon or aluminium hexite may form a nucleus to which three hexites or pentites are attached, thus:

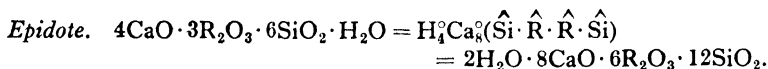
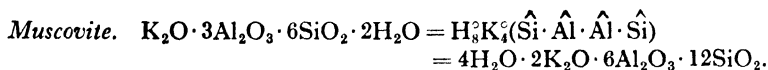


Here follow a few silicious minerals formulated according to the method of W. and D. Asch:



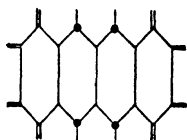
Salts of complex alumino-silicic acids are represented similarly, e.g.



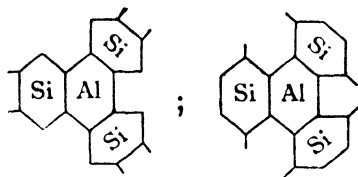
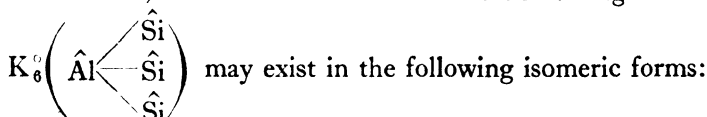


R = Al, Fe'''. .

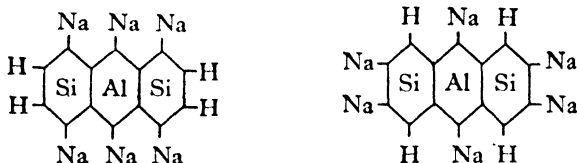
The extent and manner in which Fe''' replaces Al in this silicate is indicated in the following formula where a dot represents an iron atom:



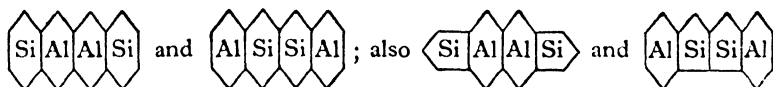
By means of the hexite-pentite (H.P.) theory isomeric silicates are foretold, and it is claimed that these exist. E.g. the compound



and the compound $H_4^{\circ}Na_8^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$ in the following:



This isomerism is called "basis isomerism". Another and more obvious kind of isomerism is called "ring isomerism", e.g.



These examples by no means exhaust the formulæ given by W. and D. Asch. The authors believe their method of formulation

to be of general application, and therefore apply it to other complex inorganic compounds, which they regard as analogous to the aluminosilicates, e.g. to complex acids such as phosphomolybdic acid.

They also develop a stereo-hexite-pentite (S.H.P.) theory of complex silicates on the same principles, so as to account for crystalline structure; and they claim that this confirms Haüy's law of relationship between crystalline form and chemical composition, and is in accord with Werner's Co-ordination Law.

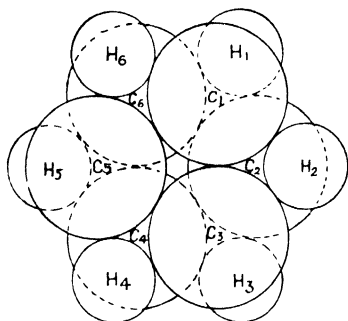
III. *The Valency Theory of Barlow and Pope*.—As an outcome of the study of crystallography, Barlow and Pope* have developed a theory of valency and chemical constitution which relates these properties in a geometrical manner to crystal form.

Every atom in a chemical compound is believed to exercise a sphere of influence, these spheres being aggregated into a stereometric arrangement which constitutes the shape of the molecule. So "a crystalline structure is a close-packed, homogeneous assemblage of the spheres of influence of the component atoms" of a compound.

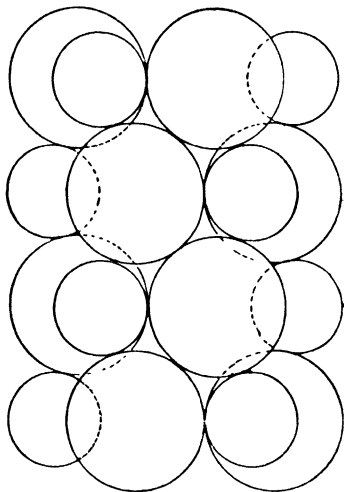
Equilibrium is due to the interaction of two forces, viz.: (1) a repellent force, which may be attributed to the kinetic energy of the atoms, (2) an attractive force of the nature of gravity. The spheres of influence of different atoms differ in size; indeed it is postulated that "the relative volumes of the spheres of atomic influence composing the various assemblages must be directly proportional to their fundamental valencies". Thus the sphere of influence of a carbon atom is approximately four times that of a hydrogen atom. The idea of bonds, that is of valency forces acting in specific directions, therefore disappears, and in place of it appears that of a force distributed equally over the surface of a sphere. Consequently a constitutional formula according to this theory consists of an assemblage of spheres of different sizes arranged in a stereometric pattern which may become a model of the crystalline form assumed by the substance. Thus for the formula of benzene, C_6H_6 , "six spheres, each of volume four, are placed in contact so that their centres lie at the apices of a regular octahedron; six spheres, each of volume about one, are then placed in six of the eight similar hollows lying round the octahedral group in such a manner that the two unoccupied hollows are diametrically opposite each other". This formula, it is claimed, is in accord with the general properties of

* *J. Chem. Soc.*, 1906, 89, 1675; 1907, 91, 1150; 1908, 93, 1528.

benzene, so far as these are expressed by the isomerism of aromatic compounds. It is then shown how such assemblages can be "close-packed" to yield a homogeneous assemblage exhibiting the symmetry and axial ratios of crystalline benzene. This is shown in the following figures:



Molecule of Benzene, C_6H_6



Crystal Structure of Benzene.

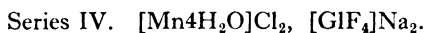
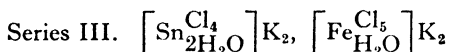
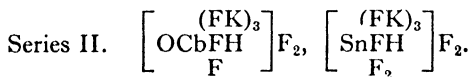
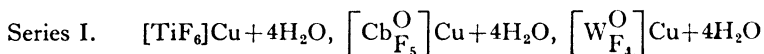
In the close-packing which is assumed to occur in the crystalline state, distortion of the sphere of influence takes place, so that the gaps originally existing between the spheres are filled. It is suggested that models of the spheres may be made of soft, solid india-rubber, which, in contact, may be distorted by pressure so that the interstitial spaces are obliterated. When processes of substitution occur the following is a condition which must be fulfilled if the original close-packing is to be maintained without remarrying. If an atom of valency $m + 1$ is introduced in place of an atom of valency m , then an additional atom of valency 1 must be brought in to fill the gap formed by expansion. This is taken to explain, for example, the existence of NH_4Cl . When the valency of N in NH_3 is increased by 1 in the formation of NH_4 , another atom of valency 1, i.e. Cl must be introduced to fill the space which otherwise would appear around the NH_4 group. Another example is furnished by comparing methylamine with ethane. When N in $CH_3 \cdot NH_2$ is exchanged for C, an atom of valency m is exchanged for one of valency $m + 1$. Therefore another atom of valency 1 must be added. i.e. not ClH_2 but CH_3 must take the place of NH_2 to form $CH_3 \cdot CH_3$,

Thus it is claimed that the new theory "endows the Frankland doctrine of valency with a real physical signification".

It is to be noticed that the spheres of influence of all univalent elements are not of exactly equal size. Consequently simple compounds of very dissimilar elements need not be isomorphous; but complex compounds of similar type are likely to be so because small differences in individual spheres will not then become apparent. Thus lead and platinum do not resemble one another in their simple compounds; but their complex compounds, such as $\text{K}_2\text{Pb}(\text{OH})_6$ and $\text{K}_2\text{Pt}(\text{OH})_6$ are isomorphous.

In the original paper a number of examples are given to show how the stereometric formulæ of compounds accord with their observed crystalline structure; especially the isomorphism of NaNO_3 and CaCO_3 as calcite is discussed, and reason is given for attributing similar structures to these two compounds in spite of the different constitutions usually attributed to them. Briefly it may be said that the theory of Barlow and Pope marks a distinct advance in our knowledge of structure, which is now becoming so well established through the electronic doctrine of valency and the work of Bragg on X-ray spectra.

T. V. Barker* criticizes Barlow and Pope for ignoring the variability of atomic volume by their hypothesis of close-packing, and for assuming valency-volume to be constant for any one element in spite of variability of valency. He then emphasizes the value of Werner's co-ordination theory in formulating the following unusual compounds which are isomorphous:



IV. *The Electro-polarity of Valency*.—It has been pointed out earlier in this book that Berzelius conceived the atoms of the elements to be possessed of two charges of electricity, positive and negative. These were situated on opposite sides of an atom and were of un-

* *J. Chem. Soc.*, 1912, **101**, 2484; also *ibid.*, 1915, **107**, 744.

equal magnitude, so that their algebraic sum represented the effective charge of the atom considered as a whole. This theory led to dualism, and was ultimately discarded because dualism was found inadequate to account for the properties of organic compounds, which required a unitary view of the molecule. It has been further pointed out that the properties of electrolytes seemed to require a dualistic view of constitution, and that the electrolytic dissociation hypothesis of Arrhenius constituted a revival of dualism in a modified form. In this theory, however, ions were electropositive or electronegative; and whilst their properties depended upon the positive or negative qualities of their constituent atoms, these atoms themselves did not necessarily possess a dual charge.

The dualism of the atom itself was, however, revived in Abegg's theory of valency: and although this theory does not require a new formulation of chemical compounds, it occupies an important place in a line of development which leads to the electronic doctrine of valency, and modern ideas regarding the electro-polarity of the atom; so it must be noticed here *.

In 1899 Abegg and Bodländer introduced "electro-affinity" as a new principle of chemical classification, this value being expressed quantitatively as the E.M.F. necessary to destroy the union between atom and electron. Four or five years later † Abegg developed a theory of valency in accordance with the periodic system, to account for the existence of molecular compounds. Just as Berzelius supposed that each atom had two charges, positive and negative, so Abegg supposed that each element had two opposite kinds of valencies, which he called normal and contra valencies. The contra valencies were never fewer than the normal valencies, but the arithmetical sum of the two kinds of valencies was equal to 8 in accordance with the 8 groups of the periodic system. According to the position of an element in a series the normal valency might be + or —, and the contra valency consequently — or +.

The following scheme shows Abegg's theory:

Group	I.	II.	III.	IV.	V.	VI.	VII
<i>Normal Valencies</i>	+1	+2	+3	+4	—3	—2	—1
<i>Contra Valencies</i>	(—7)	(—6)	(—5)	+4	+5	+6	+7

* *Zeit. anorg. Chem.*, 1899, **20**, 453.

† *Chem. Centr.*, 1903, **1**, 1203; *Zeit. anorg. Chem.*, 1904, **39**, 330.

Contra valencies may be called into play in the formation of so-called molecular compounds; sometimes, however, they are latent, or practically non-existent, as are those of groups, I, II, and III, shown in brackets in the above table.

When an element exercises either normal or contra valencies according to circumstances it is said to be amphoteric, a term introduced by Abegg; examples of amphoteric elements being, according to Abegg, H, B, Si, P, As, Sb, S, and I, which exhibit either + or - electro-affinity according to the nature of the other elements with which they combine.

Justification for Abegg's theory is found in the fact that the affinities of various elements for H and O are reciprocal, as is shown with the following pairs of compounds:

IV.	V.	VI.	VII.
SiH ₄	PH ₃	SH ₂	ClH
SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇

and when we look back upon this theory from the standpoint of the octet theory, in connexion with the electronic doctrine of valency, we can see that Abegg's views find full confirmation in the later theory.

Ramsay,* indeed, in 1908, went further than Abegg, and anticipated the electronic theory of valency as an extension of Abegg's theory. An account of Ramsay's theory will appear later in this book (p. 151).

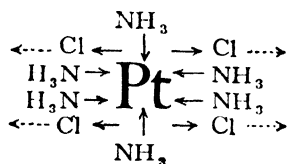
S. H. C. Briggs† has developed formulæ for platonic amines, in which the saturation of affinities is represented by arrows pointing from positive to negative, $\rightarrow$; whilst unsaturated affinity is shown by an arrow with a dotted shaft $\rightarrow$ pointing away from positive affinity and towards negative affinity, if such is present.

In the compound $(\text{Pt}6\text{NH}_3)\text{Cl}_4$ the Pt atom has positive affinity able to combine with the negative affinity of four chlorine atoms, and negative affinity which combines with six NH_3 molecules. Thus the Pt atom has 10 units of valency, 4 positive and 6 negative, which is a departure from Abegg's theory. Moreover, the four Cl atoms have positive affinity which remains unsatisfied.

* Presidential address to the London Chemical Society, *J. Chem. Soc.*, 1908, 93, 774.

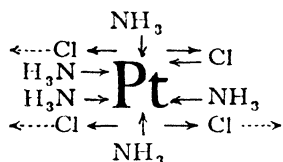
† *J. Chem. Soc.*, 1908, 93, 1564.

Consequently the compound $(\text{Pt}6\text{NH}_3)\text{Cl}_4$ is represented in the following way:

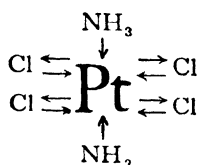


the stereometric figure, however, being a regular octahedron.

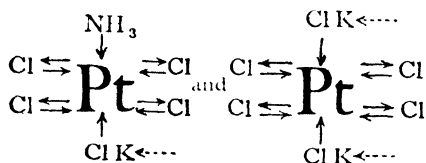
If a molecule of NH_3 is removed from this compound the Pt atom will have free negative affinity which will neutralize the free positive affinity of one of the Cl atoms. This Cl atom will then become fixed in the octahedron, i.e. it will cease to be ionized, a change which is represented thus:



When all the chlorine atoms have been fixed in this manner the compound becomes a non-electrolyte and is represented thus:



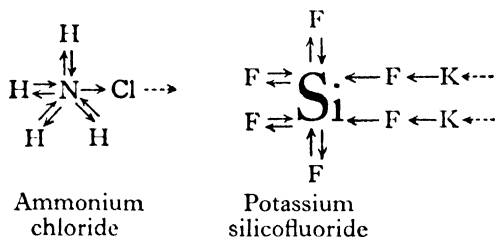
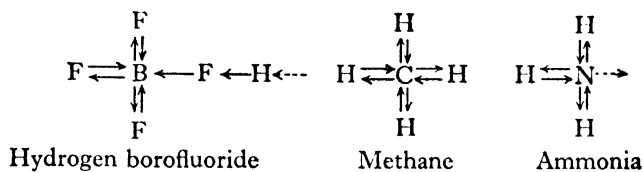
There are two more NH_3 molecules, however, to be lost, and replaced, say, by KCl ; and the compounds which are formed are represented thus:



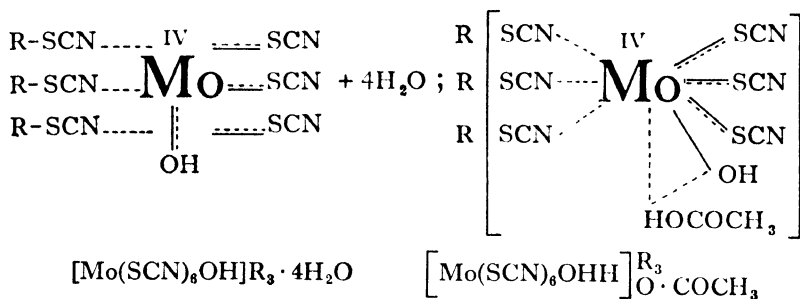
It may be remarked that Werner would have represented these compounds thus:

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$, $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$, $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$, $\text{K}_2[\text{PtCl}_6]$, the valency of the complex radical changing from +4 through zero to -2.

The following formulæ are also given by Briggs:



and the following by Maas and Sand *:



* *Ber.*, 1908, 41, 1500.

CHAPTER VI

The Electron in Chemistry

In the preceding chapters, we have considered the historical development of the use of symbols to characterize different materials dealt with in chemistry, and we have seen how great a part the atomic theory of Dalton played in giving precision to the symbolic representation of chemical operations. The adoption of the atomic theory marked a definite phase in the development of the subject by referring the chemical changes that occur in matter from the comparatively large and tangible mass which is handled, to the hypothetical, minute, invisible, indestructible, and permanent atoms of which that mass is composed. The stimulating results of this reference are seen in the rapid subsequent progress of chemical science.

We have now to consider another phase in the development of the science which arises in a manner similar to that just considered, namely, the reference of chemical changes to the operations of entities smaller even than atoms. This is rendered possible by the discovery that atoms are not indivisible and unchangeable, as Dalton supposed them to be, but are systems of electrons and protons with a complicated architecture. All chemical operations, and many physical ones, as we shall see later, alter the architecture of the atoms; sometimes an atom may even lose one or more of its constituent electrons. It is true that when such electrons are removed, the atom is not seriously injured, and its structure is only superficially altered, because at the first opportunity it regains electrons equal in number to those lost, and is thus restored to its original condition.*

Since it is found that violent treatment liberates electrons from an atom, it is a natural step to associate chemical change with the behaviour of electrons on the surface of the atom instead of with the behaviour of the atom as a whole. This association has an im-

* These remarks do not apply to actual cases of atomic disintegration, where permanent changes in the atom accompany radioactive phenomena.

portant bearing on the study of valency, and therefore on the fundamentals of chemistry. Chemistry is concerned with the linkages of atoms, one with another, and hitherto linkages have been attributed more or less vaguely to forces called valency forces. The nature of these forces is now more precisely understood to be electrical; but so little is known of the actual movements of the participating electrons that there is much scope for speculation in formulating any theory of valency. Concurrently with speculative theories, many symbolic representations of chemical change have appeared, and it is our business to discuss these in the remaining chapters of this book. We must first, however, look into the credentials of the electron, and see how it comes that this unit has attained its proud and unique place in the science of chemistry.

If we choose as our starting-point the experiments of Sir Wm. Crookes in 1880, which led to the discovery of electrons in highly evacuated electric discharge tubes, the importance of Faraday's work on electrolysis must, nevertheless, not be overlooked, because it was in this work that the first evidence of the atomic nature of electricity appeared. Thus, Helmholtz, in his Faraday lecture in 1881, said: "Now the most startling result of Faraday's law is perhaps this. If we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity." Similar views had been expressed by Clerk Maxwell in 1873, and by Johnstone Stoney in 1874. It is interesting to note that the word "electron" was first used by Johnstone Stoney to signify the definite quantity of electricity which accompanies a univalent ion during electrolysis.

The study of the conduction of electricity through rarefied gases, however, first showed that electricity could have a free existence, independent of matter. The phenomena associated with vacuum tubes are produced when a current from an induction coil is passed between two electrodes enclosed in a glass tube which has been exhausted of air. If the degree of exhaustion is appropriate, the surface of the glass glows with a phosphorescent light, usually of greenish colour, and this glow is caused by the impact of radiation which apparently is shot off in straight lines from the cathode; for when a metal plate is interposed between the cathode and the glass, a clearly defined shadow of the plate is projected on to the glass owing to the stoppage of the radiation. Experiments show that these

cathode rays have considerable penetrating power, possess a large amount of energy, and are negatively charged.

Speculations as to the nature of the cathode rays continued for nearly twenty years until Sir J. J. Thomson devised methods whereby the radiation which they composed could be resolved into separate particles whose mass, charge, and velocity could be independently determined. These experiments have clearly shown that the cathode particles, or electrons, with which they have been proved to be identical, are obtainable from all types of matter; that they are all alike in mass and charge; and that their mass is very much smaller than the mass of the lightest atom, that of hydrogen. Other experimenters, notably Millikan, have determined the mass and charge of the electron with the greatest precision, and it is now generally accepted that the mass of the electron is $1/1845$ th of that of the hydrogen atom, and that the charge it carries is 4.774×10^{-10} electrostatic units.

The symbol e is used to denote both the charge on the electron, and the electron itself. There is little confusion in the ambiguity because nothing is known about the structure of an electron, which is merely a quantity of electricity capable of an existence apart from matter, and also a constituent of all matter. The discovery that the charge on the electron is the same as that carried by a univalent ion during electrolysis naturally stimulated electronic theories of valency.

As far back as 1884, Arrhenius had put forward a hypothesis, which was generally accepted, to account for the behaviour of solutions of electrolytes. Faced with the problem of determining the extent of ionization of salts in solution, he showed that experiments on conductivity furnished the clue, if it was supposed that electrolytes were partially ionized in the process of solution, and more and more completely ionized with increasing dilution. When a salt is dissolved in water, its molecular conductivity, measured by the ratio of its specific conductivity to its concentration, increases progressively with diminishing concentration until a maximum is reached. Arrhenius suggested that the maximum value of the molecular conductivity in dilute solution corresponded with complete ionization of the salt, and that the ratio of the molecular conductivity at any other dilution to the maximum was the measure of the degree of ionization of the salt. By the use of this hypothesis, Arrhenius was able to show that the abnormally high osmotic pressure exhibited by an electrolyte was due to the dissociation of its molecules into

ions, each ion contributing to the osmotic pressure an amount equal to that due to a non-ionized molecule. The extent of the observed abnormality gave a quantitative measure of the degree of ionization, and a strong confirmation of Arrhenius's hypothesis emerged when the values so obtained were found to agree with those yielded by conductivity experiments.

As far as electrolytes were concerned, it was an obvious assumption to make, and one that led to greater precision, that the process of dissociation in solution of a binary compound was due not vaguely to the division of the available electricity in a compound between the ions according to their chemical nature, but precisely to the transference of an integral number of electrons from each atom of one of the elements to a corresponding atom of the other element.

In 1904, Sir J. J. Thomson investigated mathematically the stability and periods of oscillation of a number of electrons * arranged at equal intervals around the circumference of a circle, and applied his results to a theory of atomic structure. He supposed that the atom consisted of a number of electrons moving about in a sphere of uniform positive electrification, and created a model which, however, was discarded when it was found that the positive charges in the atom were concentrated in a minute nucleus. The number of electrons in the atom of an element was at that time undetermined experimentally, and in Thomson's original model was far too many. As will be seen below, Thomson later devised experimental methods to determine approximately the number of electrons in an atom. The paper is of interest, however, in its statement that complete ionization takes place at the moment of combination. Thus he writes †: "When atoms like the electronegative ones, in which the corpuscles are very stable, are mixed with atoms like the electropositive ones, in which the corpuscles are not nearly so firmly held, the forces to which the corpuscles are subject by the action of the atoms upon each other may result in the detachment of corpuscles from the electropositive atoms and their transference to the electronegative. The electronegative atoms will thus get a charge of negative electricity, and the electropositive atoms one of positive, the oppositely charged atoms will attract each other, and a chemical compound of the electropositive and electronegative atoms will be formed." This is a revival of the dualistic theory, and

* Called by Thomson "corpuscles".

† Thomson, *Phil. Mag.*, 1904, 7, 262.

has given impetus to attempts to apply the full theory of electrochemical dualism to organic compounds. We shall consider later the papers by Fry and others on this subject.

In 1906, Thomson showed * how evidence obtained from three widely separated classes of physical phenomena led to the conclusion that the number of electrons in an atom of an elementary substance is of the same order as the atomic weight of the substance.

This implies that all but about one-thousandth part of the mass of the atom is associated with the positive part of the atom.

In 1908, Sir Wm. Ramsay,† in his presidential address to the London Chemical Society, put forward the suggestion that the electron could be regarded as an atom of the chemical element, electricity. "Electrons possess mass; they form compounds with other elements; they are known in the free state, that is, as molecules; they serve as the 'bonds of union' between atom and atom." The symbol E was assigned by Ramsay to the electron. He says: "Let us consider the combination of sodium with chlorine to form common salt. If it be conceded that salt differs from its solution only in so far as the mobility of the solution permits of transfer of ions, the transfer of an electron from the sodium to the chlorine must take place at the moment of combination."

We note here that Ramsay's view of complete ionization as a necessary consequence of chemical combination is in harmony with that of Sir J. J. Thomson, but in conflict with the generally accepted theory of Arrhenius, which asserts that ionization increases progressively with dilution. However, the difference is not a serious one, and may be easily overcome. It may be supposed, in accordance with the views of Ramsay and Thomson, that sodium chloride is completely ionized in the process of combination, and that, when dissolved in water, the oppositely charged ions of sodium and chlorine are held in restraint by their mutual electrostatic attractions. At any given instant some pairs of ions will be close together, and other pairs will be comparatively far apart. If we imagine that a certain critical distance of separation determines whether the ions of a pair are free to respond to an electrical force and so produce electrolysis, and that the same distance approximately determines whether the ions are free to exert their osmotic pressure independently, then we have complete harmony between the two theories. A pair of ions separated by less than this critical distance will form the "non-ionized molecule" of the Arrhenius theory, will be unable

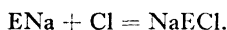
* Thomson, *Phil. Mag.*, 1906, **11**, 769.

† Ramsay, *J. Chem. Soc.*, 1908, **93**, 774.

to carry an electric current in electrolysis, and will act as one molecule as far as osmotic pressure is concerned; an ion separated by more than this critical distance from another ion of opposite sign will be mobile in an electric field, and will itself contribute to the osmotic pressure an amount equal to that of a molecule. A compound may consist in aqueous solution of ions, the positive members of which are almost entirely separated from the negative members by distances greater than this critical distance. Such a compound is a good electrolyte, and is chemically reactive. Or, a compound may be completely ionized, but the positive ions may be held so closely to the negative ions that the compound is a non-electrolyte, and sluggish in chemical activity.

Some such view as this was held as early as 1905 by Baly and Desch. In discussing the bonds of attraction between the ions of a salt solution in terms of Faraday tubes of force, following Sir J. J. Thomson, they said:* "the bonds of attraction . . . are lengthened by the solvent. When the length of the Faraday tubes is below a certain critical length the salt is "non-ionized". When the average length of the tubes of force is equal to or a little less than the critical length, a few interchanges of ions between adjacent molecules take place, and the salt is partially ionized. . . ."

Ramsay continues his discussion of the combination of sodium and chlorine thus: "Symbolized, if we write E for electron and simplify the reaction, dealing for the moment with an atom and not with a molecule of chlorine, we have



Here the electron serves as the bond of union between the sodium and the chlorine. . . . It will be noticed that the E fills the place usually occupied with a bond, thus Na—Cl. It happens providentially that the bond and the negative sign are practically the same; Na⁻Cl may be supposed to ionize thus: Na(⁻Cl), the negative charge or electron remaining with the chlorine."

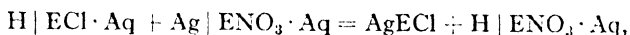
Such a theory offers no difficulties in accounting for the formation and properties of typical electrolytes such as sodium chloride, where it is easy to distinguish between the negative and positive parts of the molecule. The difficulties arise when combination between similarly charged atoms has to be accounted for. The union of two atoms of chlorine to form a molecule of chlorine is a case in point; the formation of a molecule of alcohol is another. It is the

* Baly and Desch, *J. Chem. Soc.*, 1905, 87, 784.

difficulty that all electrochemical theories have had to face: it is where Berzelius's theory came to grief, and was supplanted by Dumas's unitary theory.

Ramsay did not shirk the issue. He first discussed whether a molecule of hydrogen should be symbolized as $H-H$ or $H-H$. Since the hydrogen atom has an electron available to give to a chlorine atom when a molecule of hydrochloric acid is produced, either formula would do. In the case of chlorine, the element has apparently a reserve of electrons, for it appears to be trivalent in $KO-Cl=O$, quadrivalent in $O=Cl=O$, quinquivalent in $KO-Cl(=O)_2$, and septivalent in $KO-Cl(=O)_3$. The number of electrons available for combination may be considered to be 1, 3, 4, 5, or 7, so that when chlorine combines with itself to form Cl_2 , we have the choice between $Cl\bar{E}Cl$, ClE_3Cl , ClE_5Cl , and ClE_7Cl ; if we wish to account for all of the seven electrons in each atom we must write these formulæ $E_6Cl\bar{E}ClE_7$, $E_4ClE_3ClE_7$, $E_2ClE_5ClE_7$, ClE_7ClE_7 , respectively. Ramsay does not suggest the use of such cumbersome formulæ, but suggests ignoring the "latent" electrons, just as is done with bonds in ordinary structural formulæ: "A structural formula shows by bonds those electrons which we deem it serviceable to represent."

Ramsay develops his paper by showing how reactions may be represented by his method. Where the constituents are ionized the representation is simple; one example, the action of hydrochloric acid on silver nitrate, will serve as an illustration:

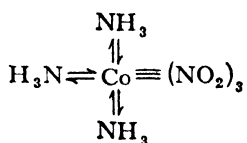


where the vertical bar denotes ionization.

In accordance with Abegg's views on valency (p. 143), Ramsay allows eight as the maximum number of valency electrons in an atom. He then arrives at a constitution of ammonium chloride which is similar to that given by Arrhenius and Werner. "The nitrogen atom, itself carrying five electrons, may receive three more from the three atoms of hydrogen in ammonia, thus: $H_3 | \equiv N$. The total number of electrons now associated with the nitrogen atom is the maximum possible, eight. If an attempt be made to add another, as in NH_4 , that proves impossible, but the nitrogen atom may part with one to the chlorine atom, already carrying seven, when it has a vacancy, as it were, which is filled from the hydrogen atom; it then becomes 'saturated'."

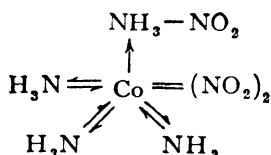
'The view that an atom may simultaneously take up and part

with an electron is further developed by Ramsay in considering the nitrites of the cobaltamines. The triamminonitrite is represented symbolically thus:

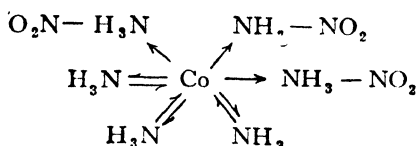


The double arrow indicates that the nitrogen of the ammonia group has both received and given up an electron.

In $\text{Co}(\text{NO}_2)_3(\text{NH}_3)_4$, where another molecule of ammonia is added, the cobalt atom gives to the nitrogen of the ammonia an electron, but does not receive one in return. The nitrogen atom cannot retain this electron, since it has already the maximum number of eight; it must lose one, and does so to one of the (NO_2) groups, converting the group into an ion. The formula proposed is thus:



A single arrow indicates the non-reciprocal transfer of an electron. The formula for hexammino-cobaltic nitrite is developed similarly:



It will be noted that there are three different symbols used in these formulæ to represent bonds, the double arrow, the single arrow, and the straight line. It is at this period in the history of chemistry that the fundamental part played by the electron in chemical change begins to be realized, and these new symbols indicate the assumed movement of electrons during chemical combination. Ramsay's explanation of the ionization of these salts is in accordance with modern views, but does not appear to be convincing from the standpoint of his own theory. He is led to the somewhat paradoxical conclusion that, whereas in a simple salt like cobalt nitrate the cobalt atom ionizes by giving up an electron to each of the three nitrate

groups, yet in the triamminonitrite the cobalt atom receives three electrons from the nitrite groups. In the absence of any reason for the different behaviour of the cobalt atom in these two cases, Ramsay's statement is not so much an explanation as a revelation of an aspect of valency which requires further attention.

The idea that an electron acts as the material which binds atoms together was developed a stage further by Stark,* and by Kaufmann.†

Stark pictured the atom as consisting of two parts; one part was a ring or sphere in which the positive charges were embedded,

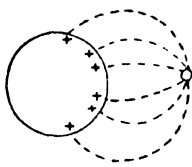


Fig. 1

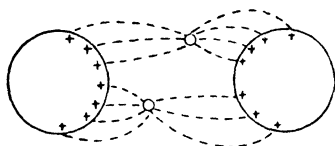


Fig. 2

the other consisted of electrons which were detachable, and were regarded as valency electrons. Lines of force emanating from a valency electron end on positive charges either wholly in the same atom, or else partly in the same atom and partly in another. If the lines from an electron end on the same atom, a configuration like that shown in fig. 1 is obtained; and the valency electron is supposed to be unsaturated. If, however, a second neutral atom approaches, a diatomic molecule is formed by the deflection of some of the lines of force from the electron on to the second atom; the valency electron of the second atom similarly shares its lines of force between the two atoms, according to the scheme shown in fig. 2. A third case was considered by Stark, when under different circumstances the approach of an atom weakened the attachment of certain electrons by the repulsion of neighbouring electrons. Fig. 3 shows a group of three atoms held

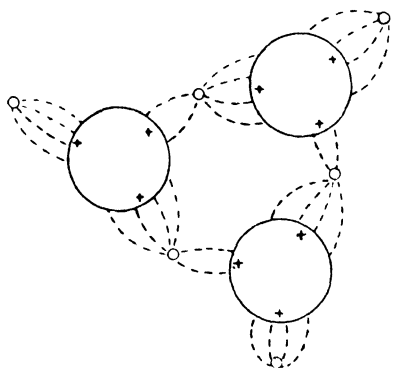


Fig. 3

* *Phys. Zeitsch.*, 1908, 9, 85; *Prinzipien der Atomdynamik III, Die Elektrizität im chemischen Atom.*

† *Phys. Zeitsch.*, 1908, 9, 311.

together by three electrons, and in addition three electrons which are more loosely bound and may be split off in dissociation. Historical interest in Stark's work is mainly centred in one of his pictures of a chemical bond, viz., that in fig. 2. Here the bond is represented as the sharing of a pair of electrons by two atoms. It

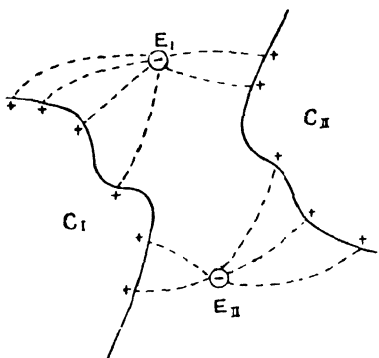


Fig. 4

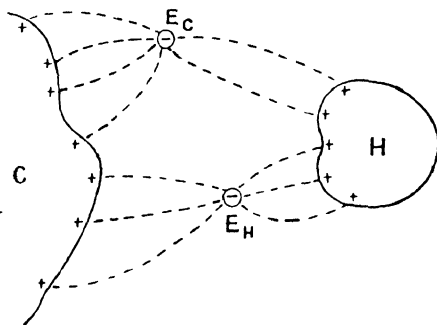


Fig. 5

will be seen later that Lewis has developed a simple and comprehensive theory of valency, which reconciles the unitary and dualistic theories, by assuming that the chemical bond is always to be so represented. Figs. 4 and 5, which are Stark's diagrams of the carbon-carbon bond and the carbon-hydrogen bond respectively, further illustrate this conception of the sharing of bonds.

Kaufmann* put forward views somewhat similar to those of

Stark. He represented the single bond by the figure $A \begin{array}{c} \diagup \circ \diagdown \\ \diagdown \circ \diagup \end{array} B$,

the small circles being electrons which are shared between the

atoms A and B. A double bond is indicated as $A \begin{array}{c} \diagup \circ \diagdown \\ \diagdown \circ \diagup \\ \diagup \circ \diagdown \\ \diagdown \circ \diagup \end{array} B$,

showing conformity to the generally accepted modern view that a pair of electrons are shared for each chemical bond. The lines of force from the two outer electrons involved in a double bond are extended farther into space than those concerned in a single bond, and the stray field of force so produced accounts for the greater reactivity of unsaturated compounds containing a double bond than of saturated compounds which have no double bond.

* *Loc. cit.*

Kaufmann extended his theory to embrace Thiele's partial valency theory. By assuming that an electron may be held simultaneously by more than two atoms, he necessarily supposed the divisibility of

valency. Thus, in the group $A \begin{array}{c} \swarrow \searrow \\ B \\ \swarrow \searrow \\ \circ \end{array} C$, the sign $\longleftrightarrow$ represents a pair of saturated electrons, and the small circle a loosened electron. Kaufmann's formula for benzene is shown in fig. 6, and is really an electronic representation of the one suggested by Thiele, and shown on p. 94. This formula, and that of Stark shown in fig. 7, are noteworthy as the forerunners of others based on the electronic theory.

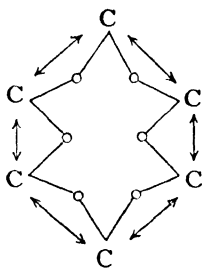


Fig. 6

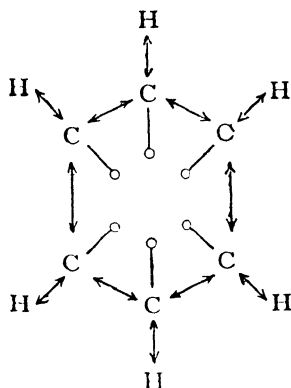


Fig. 7

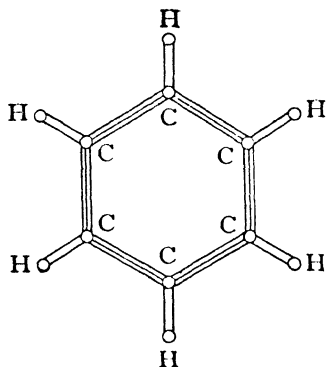
In 1914, Sir J. J. Thomson* discussed the forces between atoms, and chemical affinity, from the point of view of electrical charges. The atom is regarded by Thomson as a mixture of negatively electrified corpuscles and positive electricity, and combination between two atoms occurs when a tube of force from a corpuscle of each atom extends to the positive portion or core of the other atom. Each bond in the structural formula of a compound is shown by two lines, one line representing a tube of force going from an atom and the other a tube entering the atom. This widens the conditions of valency for a compound. For most of the ordinary saturated compounds, the only difference is to double the number of lines in the structural formulæ, regarding two lines, i.e. two tubes of force, as equivalent to the chemical bond; but by postulating that a valency is saturated when each atom sends out as many tubes of force as it receives, whether or not it sends out a tube to the same atom as it receives one from, it is possible to represent such a molecule

* Thomson, *Phil. Mag.*, 1914, 27, 757.

as H_2 as an ordinary valency molecule with hydrogen univalent, a result which the usual theory cannot achieve. Thus, the formula

$\begin{array}{c} H \\ \diagup \quad \diagdown \\ H \triangle H \end{array}$ shows each atom as the origin and termination of a tube of force, and satisfies the condition above, even though the hydrogen atom has only one free corpuscle.

In a similar way, Thomson derives the structural formula for benzene shown below. The ring is quite symmetrical, and each union between two carbon atoms is unlike the single, the double, or the triple bond; in fact, the linkage may be said to correspond to a bond and a half.



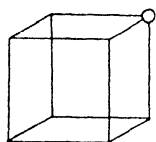
Lewis's Theory of Valency.—The part played by the electron in valency was given greatest precision by the theory of Lewis which was first published in 1916.* In this paper, Lewis contrasted the difference in properties between the extreme polar and the extreme non-polar types of chemical compounds. The essential difference between the two is that whereas in non-polar compounds the electrons are held in great constraint, in polar compounds weakly attached electrons be-

come displaced from their former positions in the atom, and in extreme cases are transferred entirely to another atom. Although the two types show great differences in extreme cases, the distinction between them is only one of degree, and not of kind, so that the theory embraces both types of compound. The fact that the algebraic difference between the numerical values of the maximum negative and positive valencies of an element is usually eight and never exceeds eight—a fact discovered independently by Abegg (p. 143)—led Lewis to picture a cubical atom, in which the small circles represent electrons in the outer shell of the neutral atom, which consists of a kernel and an outer shell. The kernel remains unaltered in chemical changes, and carries an excess of positive charges corresponding numerically to the number of the group in the periodic table to which the element belongs: the outer shell contains electrons equal in number to the excess of positive charges of the kernel,

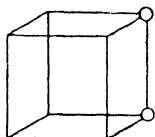
* Lewis, *Jour. Amer. Chem. Soc.*, 1916, 762.

but during chemical change this number may vary between 0 and 8, and the atom tends by gain or loss of electrons to hold eight of these arranged symmetrically at the eight corners of a cube.

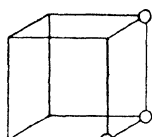
Lewis considered the kernel to be of sufficient importance to merit a separate symbol, and proposed that the common symbol



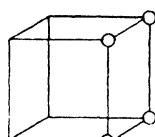
Li



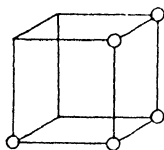
Be



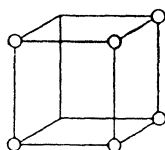
B



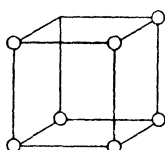
C



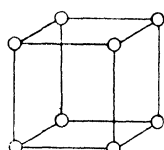
N



O



F



Ne

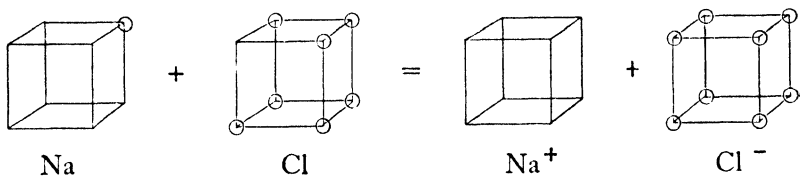
of the element should be printed in a different type to represent the kernel. Thus **Li** would be equivalent to Li^+ . In the case of the inert gases, the outer shell of eight electrons is included in the kernel, so that, for example, **Ne** = Ne. The next element, sodium, begins a new outer shell, so that **Na** = Na^+ , **Mg** = Mg^{++} , and so on.

The Rule of Eight.—The tendency of atoms to hold eight electrons is best shown by using formulæ which include the valency electrons. Denoting the electron by **E**, it is found that all compounds in which each element is exerting its maximum valency give formulæ with **E** as multiples of eight; thus $\text{NH}_3 = \text{NH}_3\text{E}_8$, $\text{H}_2\text{O} = \text{H}_2\text{OE}_8$, $\text{NaNO}_3 = \text{NaNO}_3\text{E}_{24}$, $\text{MgCl}_2 = \text{MgCl}_2\text{E}_{16}$, $\text{K}_2\text{CO}_3 = \text{K}_2\text{CO}_3\text{E}_{24}$.

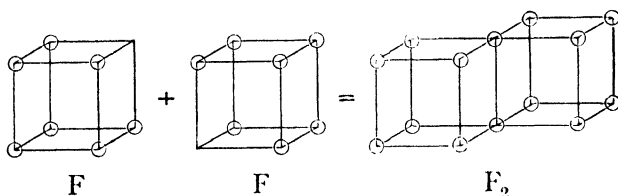
The Rule of Two.—In compounds in which the elements do not all exert their maximum valencies, the number of electrons is not as a rule a multiple of eight, but is in almost all cases an even number; thus $\text{SO}_2 = \text{SO}_2\text{E}_{18}$, $\text{NaClO} = \text{NaClOE}_{14}$, $\text{C}_6\text{H}_6\text{O} = \text{C}_6\text{H}_6\text{OE}_{36}$. Particular stress is laid by Lewis on the stability of the electron pair; for of some hundred thousand known compounds, all but a few contain an even number of electrons. The few exceptions are very reactive, and tend to pass into substances with an even number

of electrons, e.g. $\text{NO} = \text{NOE}_{11}$, $\text{NO}_2 = \text{NO}_2\text{E}_{17}$, $\text{ClO}_2 = \text{ClO}_2\text{E}_{19}$, $(\text{C}_6\text{H}_5)_3\text{C} = (\text{C}_6\text{H}_5)_3\text{CE}_{91}$.

The Sharing of Electrons by Atoms.—Perhaps the most far-reaching and fruitful idea in this paper by Lewis is the conception of the interpenetrability of two atomic shells, whereby an electron may form a part of the shell of two different atoms, and cannot be said to belong to either one exclusively. A pair of electrons shared by two atoms is equivalent to a chemical bond; and there is no other kind of chemical bond. The combination between sodium and chlorine to form an extreme polar type would be represented by the complete transference of an electron from the sodium atom to the chlorine thus,

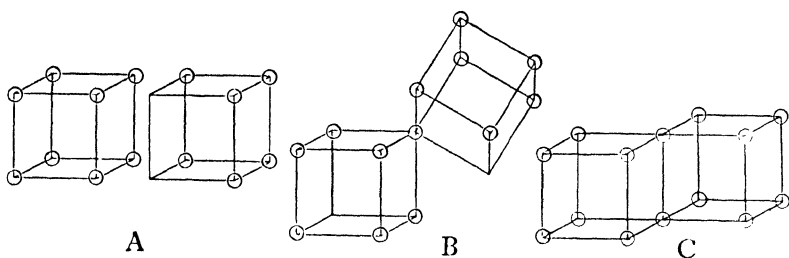


and the molecule would be held together by the electrostatic attraction of its constituent ions. The combination of two fluorine atoms to form an extreme non-polar type of molecule, would, on the assumption of electron sharing, be represented thus,



The contrast between these modes of union has been emphasized by Langmuir,* who has differentiated between the two types of valency exhibited by calling them *electrovalency* and *covalency* respectively. Lewis, however, has been more anxious to harmonize the two main theories of chemical union into one generalization which accentuates the stability of the electron pair. He illustrates his theory of the progressive change from the one extreme of complete ionization to the other extreme of complete non-polarity by reference to the pictures of the iodine molecule following:

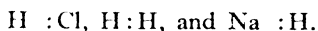
* Langmuir, *Jour. Amer. Chem. Soc.*, 1919, **41**, 868.



A represents the one extreme of a completely ionized molecule, an electron having been transferred from one atom to another so as to form the two oppositely charged ions I^- and I^+ ; C represents the completely non-polar molecule I_2 where two electrons forming a pair are equally shared between the two atoms; and B represents one of an infinite number of states intermediate between A and C where one atom has a greater share of the electron pair than the other. In liquid iodine all the molecules are not in the same state, but examples of all three types are present; in different solvents the polarity of iodine is different because some solvents rather than others favour the production of the more polar forms.

The continuity between electrovalency and covalency is a distinguishing feature of the Lewis theory, and at once differentiates it from those theories which postulate ionization as a necessary prelude to all chemical combinations, and from those which accentuate the difference between electrovalent and covalent compounds.

The symbols used by Lewis to express the idea of chemical union by means of a pair of electrons is a colon, thus Cl_2 is written as $Cl:Cl$. The position of the symbol may be used to indicate which atom possesses the greater share of the electron pair, thus



The symbol for the kernel may be used, in which case all the valency electrons would be shown, e.g. $:\ddot{Cl}:\ddot{Cl}:$ and $H:\ddot{I}:$.

One very important consequence of this representation of valency is the modification of the relationship between the numerical valency of an element and the number of bonds which must be shown in a structural formula of a compound containing that element. Previous to Lewis's theory, a bivalent element was always shown with two bonds; if not, it was supposed to be unsaturated. On Lewis's theory, however, oxygen may be shown to be held to another element by

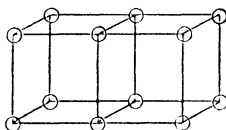
only one pair of electrons (representing a single bond) and yet both

elements may be completely saturated. Thus $\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:}\ddot{\text{X}}\text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} \end{array}$ repre-

sents the perchlorate, the sulphate, the orthophosphate, or the orthosilicate ion according as X is Cl, S, P, or Si respectively. In all cases each oxygen atom has a complete shell of eight electrons, and is held to the central atom by one pair of electrons only, i.e. by one bond.

In this way, structural formulæ found to be so useful in organic chemistry may be employed to represent inorganic compounds without the ambiguities and paradoxes which arose when graphic formulæ with bonds were used. Hitherto, graphic formulæ had been constructed to accord as far as possible with the recognized valencies of the elements, e.g. oxygen two, and phosphorus three or five. These numbers are determined by the groups in the periodic table in which the elements are found. It is one of the supreme achievements of Lewis to have given new rules on which to base graphic formulæ, viz. the rule of two and the rule of eight, which not only simplify their construction but remove the ambiguities and inconsistencies which formerly existed. We have just seen, for example, an illustration in the orthophosphate ion, where the valency of oxygen is one, and that of the phosphorus four.*

The double bond.—The double bond is represented by the sharing of two pairs of electrons, e.g. the oxygen molecule is represented thus:

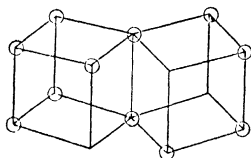


Double bonds are usually associated with reactivity, so that the above structure apparently tends to open out,† giving the following more

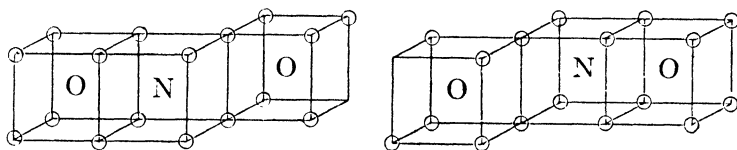
* It may be questioned whether valency means the capacity of an element to combine or is manifested only after the element has combined. Whereas the former meaning is the one presented to the student of chemistry in his first year, it is apparent that the word valency can have a more extended meaning and be used in connexion with an element or radical after it has combined with another element or group of elements to form a compound, and so denote the number of bonds which hold the element in that compound. Lewis, in effect, pointed out that these two ways of evaluating the valency do not always give the same result.

† This way of representing double bonds does not suggest reactivity, as no reason for the opening out of the structure is apparent. We shall see later that Lewis has discarded the cubic arrangement of the electrons in favour of the familiar tetrahedral form, where a

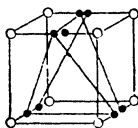
reactive form to a proportion of the molecules:



Each atom in this figure has now an unpaired electron and has therefore the reactivity of a substance with an odd number of electrons. The equilibrium between the above forms of oxygen is comparable with that between N_2O_4 and NO_2 , the latter being a molecule with an odd number of electrons (see p. 160). The following figure shows two molecules of NO_2 according to the cubic atom theory, with two corners unoccupied by electrons; and it indicates how the approach of the two molecules gives rise to N_2O_4 .



The tetrahedral atom.—Lewis lays greater stress on the stability of the electron pair than he does on the grouping of eight, and, although the ease with which a large number of compounds can be represented by cubes led him initially to use models with this structure, the generally accepted tetrahedral shape of the carbon atom caused him to discard the cubic model while still retaining the affinity of an electron pair. The transition from the one model to the other is represented thus:



Each pair of electrons (shown by circles) is attracted together so that it forms a corner of a tetrahedron. The triple bond, i.e. the sharing by two atoms of three pairs of electrons, which cannot be represented on the cubic model, is represented here in a simple way by the sharing of a face.

pair of electrons is situated at each corner of a tetrahedron. A double bond is there represented by an edge common to two tetrahedra, and the tendency for such a structure to open out is more feasible.

In developing his theory, Lewis * has discarded models altogether, and, accepting the Bohr theory of the atom, uses the symbol of the colon to represent a pair of electrons or electronic orbits. The colon represents in the most general way a pair of electrons shared between two atoms. No attempt is made to give a three-dimensional figure. Thus the two forms of oxygen given above are represented by $:\ddot{\text{O}}::\ddot{\text{O}}:$ and $:\ddot{\text{O}}:\ddot{\text{O}}:$, which show two extreme states of the double bond, the entirely closed and the completely broken.

Acetylene with its triple bond would be represented by Lewis as $\text{H}:\text{C}:::\text{C}:\text{H}$, and visualized as two tetrahedra having a face in common. However, Lewis has pointed out the greater stability of compounds with triple bonds over those with double bonds†, and, rather than accept a configuration suggesting greater instability, he is prepared to sacrifice his "rule of eight" and assume that the alternative structure $\text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\text{H}$ is possible. This implies a single bond between the two carbon atoms, and that there is a group of only six electrons round each atom. Again, the two formulæ represent extremes, the properties of acetylene being best explained by assuming a tautomeric equilibrium between these and intermediate configurations.

We have now indicated the main points in Lewis's original epoch-making paper, and before considering how the ideas there put forward have been developed by himself and others, it remains for us to emphasize the far-reaching achievements of his theory, and to summarize the main contributions which have been made by it to the study of valency.

The Lewis theory summarized.—(1) A neutral atom is composed of a kernel which is unaffected by chemical change and a shell of electrons equal in number to the group number of the element in the periodic table.

(2) During chemical change, the number of electrons in the shell may vary from 0 to 8; this variation may result from the sharing of pairs of electrons by adjacent atoms or, in an extreme case, by the complete transference of one or more electrons to another atom or atoms, in which case the atoms in the molecule are held together by electrostatic attraction. This harmonizes the electrochemical theories of valency (e.g. that of Berzelius) with unitary theories (e.g. that of Dumas).

* Lewis, *Valence, and the Structure of Atoms*, Amer. Chem. Soc. Monograph Series, 1923.

† Ethylene, for example, combines much more rapidly with bromine than does acetylene.

(3) Special instability of compounds is associated with an odd number of electrons; nearly all compounds have an even number.

(4) By making a pair of electrons, shared between two atoms, the equivalent of a bond, the theory embraces without change the bond theory which has proved so successful in organic chemistry; and whereas the bond theory when applied to inorganic compounds has proved ambiguous and indecisive, the theory of shared pairs of electrons has given simple formulæ indicating complete saturation of valencies; for example, a simple cubic model can be arranged for the sulphate ion by giving the central sulphur atom a covalency

of four and each oxygen atom a covalency of one, thus
$$\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:}\ddot{\text{S}}\text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} \end{array}$$

Each atom has a group of eight electrons round it, and is therefore

saturated, whereas written on the bond theory
$$\begin{array}{c} \text{O} \\ | \\ \text{O}-\text{S}-\text{O} \\ | \\ \text{O} \end{array}$$
 the

attributing of four bonds to sulphur and only one to each oxygen atom would seem an *ad hoc* proceeding without any justification.

These statements indicate the main points of the Lewis theory; and before considering the latest development of it, we will consider how the theory has been extended by others. The most notable extension has been that of Langmuir.

Langmuir's theory.—Whereas the theory of Lewis was confined to the lighter elements occupying the first half of the periodic table, Langmuir attempted an extension to cover the whole table. In doing so, he * took as a starting-point the numbers of electrons which make up the atoms of the inert gases. These gases are uniquely stable and do not enter into chemical combination; therefore it can be safely assumed that their planetary electrons are in a very stable configuration.

The precise number of electrons in the atom of an element had previously been determined by researches in three different fields of work, the group displacement law of radioactive elements, the scattering of α particles when passing through matter, and the wave-

* Langmuir, *Jour. Amer. Chem. Soc.*, 1919, **41**, 868.

lengths of the characteristic X-rays emitted from the elements.* Further, the experiments on the scattering of α particles showed not only the number of electrons but their location, for they showed that the positive charges of the atom are located in a nucleus which is extremely minute in proportion to the size of the atom; so that, in order to have a neutral atom, there must be electrons external to the nucleus and equal in number to the number of positive charges in the nucleus. Hence arose the suggestion of Rutherford that the atom was like the solar system, the positive nucleus corresponding to the sun, and the electrons to the planets. It was immediately shown by Bohr that, by the use of such an atomic model for hydrogen, a simple quantitative account of the relationships between the wave-lengths of the lines of the hydrogen spectrum could be given.

The atomic numbers of the elements are their ordinal numbers when the elements are arranged in the sequence in which they appear in Mendeléeff's periodic table, e.g. hydrogen 1, helium 2, lithium 3, &c. The atomic number of an element is also equal to the number of planetary electrons in an atom of the element. We find that the atomic numbers of the inert gases are helium 2, neon 10, argon 18, krypton 36, xenon 54, and radon 86. Rydberg showed that these numbers are obtained from the simple series

$$N = 2(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 + \dots);$$

for expanding, this becomes

$$N = 2 + 8 + 8 + 18 + 18 + 32 + \dots,$$

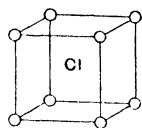
and so gives the number of elements possible in each period of the Mendeléeff table. This suggestion is in agreement with that of the atomic numbers of the elements as determined experimentally by Moseley and others.

Langmuir's theory was developed by the aid of eleven postulates. The first seven dealing with the arrangement of electrons in atoms were prematurely precise, and, being not only entirely speculative but in conflict with spectroscopic evidence, have been abandoned. The remaining four postulates deal with the mechanism of chemical combination, and cover the ideas of the Lewis theory already discussed. In his development Langmuir emphasizes the prevalence of the group of eight electrons in nearly all compounds of elements of atomic number less than 20; this group he calls the octet, a cir-

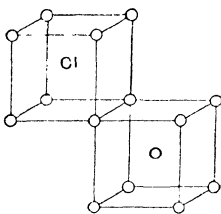
* An account of these researches is beyond the scope of this book, but may be found in another volume of this series, *The Structure of Matter*, by Cranston.

cumstance which gives rise to the name of the theory, "the octet theory of valency".

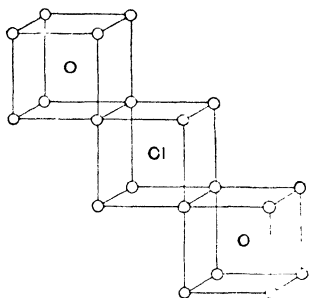
Langmuir distinguishes between two types of valency, which he calls electrovalency and covalency. The former can be subdivided further into positive and negative valency. Positive electrovalency represents the number of electrons in the outer shell of an atom; negative electrovalency represents the number of electrons required in the outer shell for the completion of that shell to the configuration



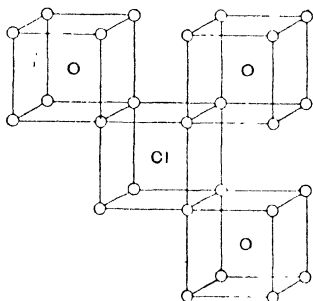
Chloride of Ion: $e = 8$, $8n = 8$; $B = 0$.



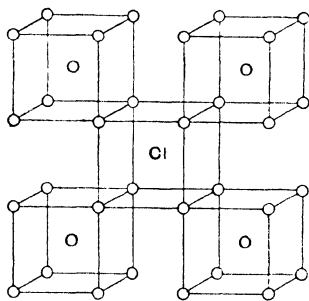
Hypochlorite Ion: $e = 14$; $8n = 16$, $B = 1$.



Chlorite Ion: $e = 20$; $8n = 24$; $B = 2$



Chlorate Ion: $e = 26$; $8n = 32$; $B = 3$



Perchlorate Ion: $e = 32$; $8n = 40$, $B = 4$.

of that of the next inert gas. These are definite conceptions, and for the lighter elements correspond exactly to Abegg's normal and contravalencies. Covalency, on the other hand, is the number of pairs of electrons that the atom, when in combination with other atoms, shares with these atoms. The number is not a definite one, nor has it any fixed relation to the number of electrons in the shell of the atom originally. Langmuir points out that the lack of success of the bond theory in inorganic chemistry is due to the attempts that are made to construct formulæ in which elements are assigned their usual electrovalency; thus, to take one example, no formulæ for the oxyacids of chlorine which can be fully justified exist on the older

theory. On the octet theory, chlorine has a negative electrovalency of one in hydrochloric acid because it has received one electron from hydrogen, and so completed its octet and attained the electron configuration of argon. In the oxyacids, hypochlorous, chlorous, chloric, and perchloric, however, chlorine has covalencies of 1, 2, 3, and 4 respectively. The figure on p. 167 shows the structures of these ions on the octet theory.

It will be noted that the chloride ion, not the chlorine atom, can add 1, 2, 3, or 4 oxygen atoms, and that the covalency of oxygen is one throughout. The oxygen atoms contribute no electrons to the union, but take a share of a pair of electrons belonging to the chlorine atom when these are available. Four such pairs are available in the chloride ion, and only four, which explains the existence of the perchlorate ion, and the non-existence of more highly oxidized ions. If a neutral oxygen atom can attach itself to another atom by covalency without contributing to the electron pair that constitutes the union, it is apparent that the oxygen atom in such combinations can be regarded as negatively charged at the expense of the other atom. It is thus possible to indicate in a compound where positive and negative charges reside, and to assert the existence of "intra-molecular ionization". The properties of the compound in subsequent reactions may then be referred to the existence of electrically charged portions of the molecule. Many theories of this nature have been developed from this conception, some of which will be dealt with later.

Although the covalency of an element may vary in different compounds containing that element, there is no ambiguity about its numerical value in a compound provided it is assumed that all the atoms finally have octets of electrons round them. It is a matter of counting the total number of electrons available from all the atoms, e , and the number of octets required, n . The difference between $8n$ and e must be equal to the number of electrons that are shared, i.e. the number that are counted twice in determining $8n$. As two shared electrons constitute one covalent bond, we get the number of covalent bonds, B , in a compound from the simple equation $B = \frac{1}{2}(8n - e)$. It will be observed that only the number of bonds is given, not their location, e.g. applying the equation to the cyanate ion CNO' , we get that $B = 4$, but we can arrange the atoms in any way we please as long as four pairs of electrons are shared.

In a later paper, Langmuir* has modified his theory and made it

* Langmuir, *Science*, 1921, 54, 59.

more general by adopting only three postulates. He still recognizes three distinct types of valency, viz. positive valency, the number of electrons an atom can give up; negative valency, the number of electrons an atom can take up; and covalency, the number of pairs of electrons an atom shares with its neighbours. The fundamental cause of chemical action is the tendency of electrons in atoms to adopt certain configurations as expressed by the three postulates.

The first postulate states: *The electrons in atoms tend to surround the nucleus in successive layers containing, 2, 8, 8, 18, 18, and 32 electrons respectively.* This postulate is based on the Rydberg series (p. 166), and on the assumption that, in the building up of the elements from the lighter to the heavier, the atoms of the inert gases are to be regarded as having completed layers of special stability which are retained unchanged in heavier elements. For example, the structure of the atom of argon is represented by three layers consisting of 2, 8, and 8 electrons respectively; the atom of bromine would possess the same three layers of 2, 8, and 8 electrons plus a fourth layer containing 17 electrons. The chemical properties of bromine would be summarized by stating that the atom tended to complete the fourth layer by the acquisition of another electron.

It may be mentioned here that this assumption of the distribution of electrons in atoms is in conflict with spectroscopic evidence; and it has been shown by Bohr that the configuration of the electrons in the argon atom, for example, is not preserved in all the heavier atoms. Whereas in Bohr's arrangement the electrons in the argon atom are grouped 2, 8, and 8, the corresponding grouping for bromine would be 2, 8, 18, and 7, showing that the accumulation of electrons in the fourth group increases the accommodation for electrons in the third. In a similar manner the arrangement of the 86 electrons of radon is given by Bohr as 2, 8, 18, 32, 18, 8.*

The remaining postulates of Langmuir are: *Two atoms may be coupled together by one or more duplets held in common by the completed sheaths of the atoms,* and, *The residual charge on each atom and on each group of atoms tends to a minimum.*

The former expresses the leading idea of the theory of Lewis already discussed; the latter deals with those compounds where the tendency expressed in Postulate 1 could only be satisfied by the

* Bury, from chemical evidence (*J. Amer. Chem. Soc.*, 1921, **43**, 1602) arrived independently at a grouping of electronic layers similar to that of Bohr. According to both Bohr and Bury, the number of electrons in the outer shell of the atom of an element never exceeds eight, but the number in the next inner shell may vary for those elements in the long periods which show variable valency.

production of ions carrying very large charges, e.g. the atom of nickel could attain the inert gas configuration of argon only by losing 10 electrons and forming an ion so highly charged as to be obviously incapable of existence.

A detailed discussion of these postulates, however, is beyond the scope of this book, though, in a later chapter, when other theories have been discussed, they will be referred to in contrasting the formulæ of certain compounds. It should be mentioned, however, that there are many cases which are not covered by the theory of Lewis and Langmuir. No explanation is afforded of the combination between electropositive metals, i.e. of the vast number of inter-metallic compounds, and special structures and modifications of the theory have to be brought into account for N_2 , CO, NO, CN' , H_4O_2 (in ice), H_2F_2 , &c.

We shall now turn to consider some theories which, though electronic, are not based on the structure of the atom.

CHAPTER VII

Extreme Dualistic Theories of Valency

It may be noted that whereas the isolation of the electron, and the realization of the fundamental part it plays in chemical change—both due to Sir J. J. Thomson—have given rise to nearly all our modern theories of valency, there are those * who believe that valency can best be studied without considering the ultimate nature of chemical affinity and without concern for the constitution of the atom. Of these, Fry † has given in some detail a hypothesis of valency based on the early suggestion of Sir J. J. Thomson that the “bond” of the chemist may be regarded as indicating a unit Faraday tube. From this point of view the symbol of the bond assumes an added significance, since one end corresponds to a positive and the other to a negative charge, through the transference of an electron from the one atom to the other.

The electronic formulæ of Fry can only be justified if they possess greater significance in interpreting and correlating chemical facts than do the customary structural formulæ; for they are derived by postulating the transference of electrons from one atom to another in compounds which are not only non-electrolytes but which show no direct evidence of unequal charge distribution. Let us then consider Fry's contribution to the subject.

Fry's electronic conception of valency.—Fry's views are based on those formulated by Sir J. J. Thomson in 1903 (Silliman Lectures), which are of such fundamental importance and historic interest that they may be quoted rather fully:

“On the view that the attraction between the atoms in a chemical compound is electrical in its origin, the ability of an element to enter into chemical combination depends on its atom having the power of

* Falk and Nelson, *J. Amer. Chem. Soc.*, 1910, **32**, 1637; Fry, *ibid.*, 1912, **34**, 664; Stieglitz, *ibid.*, 1914, **36**, 272; Jones, *ibid.*, 1914, **36**, 1268; Noyes, *ibid.*, 1920, **42**, 2173; 1922, **44**, 1630; 1915, **37**, 189; &c.

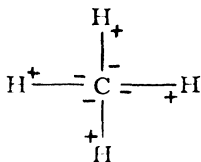
† Fry, *The Electronic Conception of Valence and the Constitution of Benzene*, Longmans, 1921.

acquiring a charge of electricity. This, on the preceding view, implies either that the uncharged atom is unstable and has to lose one or more corpuscles before it can get into a steady state, or else that it is so stable that it can retain one or more additional corpuscles without any of the original corpuscles being driven out. If the range of stability is such that the atom, though stable when uncharged, becomes unstable when it receives an additional corpuscle, the atom will not be able to receive a charge either of positive or negative electricity, and will therefore not be able to enter into chemical combination. Such an atom would have the properties of the atoms of such elements as argon or helium.

“The view that the forces which bind together the atoms in the molecules of chemical compounds are electrical in their origin, was first proposed by Berzelius; it was also the view of Davy and of Faraday. Helmholtz, too, declared that the mightiest of chemical forces are electrical in their origin. Chemists in general seem, however, to have made little use of this idea, having apparently found the conception of ‘bonds of affinity’ more fruitful. This doctrine of bonds is, however, when regarded in one aspect, almost identical with the electrical theory. The theory of bonds when represented graphically supposes that from each univalent atom a straight line (the symbol of a bond) proceeds; a bivalent atom is at the end of two such lines, a trivalent atom at the end of three, and so on; and that when the chemical compound is represented by a graphic formula in this way, each atom must be at the end of the proper number of the lines which represent the bonds. Now, on the electrical view of chemical combination a univalent atom has one unit charge, if we take as our unit of charge the charge on the corpuscle; the atom is therefore the beginning or end of one unit Faraday tube; the beginning if the charge on the atom is positive, the end if the charge is negative. A bivalent atom has two units of charge and therefore it is the origin or termination of two unit Faraday tubes. Thus, if we interpret the ‘bond’ of the chemist as indicating a unit Faraday tube, connecting charged atoms in the molecule, the structural formulæ of the chemist can be at once translated into the electrical theory. There is, however, one point of difference which deserves a little consideration: the symbol indicating a bond on the chemical theory is not regarded as having direction; no difference is made on this theory between one end of a bond and the other. On the electrical theory, however, there is a difference between the ends, as one end corresponds to a positive, the other to a negative charge.”

In applying these views, Fry adopts the symbol $\ominus$ for the electron. Thus, in the combination of the two univalent atoms, X and Y, where X tends to lose an electron and Y to gain one, we have the reactions $X - \ominus \rightarrow \overset{+}{X}$ and $Y + \ominus \rightarrow \overset{-}{Y}$ yielding the compound XY which would be represented by $X^+ \text{---}^- Y$, a formula which would indicate the polarities of the bond of attraction or tube of force between the atoms, i.e. one end of the bond is +, the other —.

The distinction between electrolytes and non-electrolytes on this theory is relative only. If XY is a salt-like compound, and is placed in a solvent, its bonds of attraction are lengthened by the solvent.* When the length of the Faraday tube is less than a certain critical value, the molecule is non-ionized; when the length exceeds that value the molecule is ionized. It will be seen later that electronic formulæ are given to compounds like methane, e.g.



so that it must be presumed that in such compounds the Faraday tubes are always very short.

It is as well to realize early that this theory is boldly applied to account for elementary molecules; thus the molecule of hydrogen is formulated $\text{H}^+ \text{---}^- \text{H}$. The theory may be regarded as a revival of the dualistic theory of Berzelius, but whereas Berzelius assumed that atoms of elements normally possessed an excess of either positive or negative electricity, this theory assumes that all reactions involving the decomposition of molecules, even elementary molecules, are preceded by an ionization of the parts of the molecules. This view is consistent with views expressed by Helmholtz † and by Noyes, ‡ and is supported by the observations of Sir J. J. Thomson § on the conductivity of elementary gases at high temperatures.

Fry has developed a rule which gives the number of ways in which an atom may function electronically in terms of the number of valencies possessed by that atom. A univalent atom may either

* Baly and Desch, *J. Chem. Soc.*, 1905, 87, 784.

† Helmholtz, *J. Chem. Soc.*, 1881, 39, 303.

‡ Noyes, *J. Amer. Chem. Soc.*, 1901, 23, 460.

§ Thomson, *Corpuscular Theory of Matter*, pp. 130-31, 1907.

gain or lose an electron, and may thus function in two ways, e.g. the hydrogen atom may become under different circumstances either $\overset{+}{\text{H}}$ or $\bar{\text{H}}$. A bivalent atom may function in three ways, viz. through the gain of two electrons, through the loss of two electrons, or through the simultaneous loss of one electron and the gain of another; thus,

the oxygen atom may become $\overset{-}{\text{O}}$, $\overset{+}{\text{O}}$, or $\overset{+}{\text{O}}\overset{-}{\text{O}}$. The rule is thus: "An atom whose valency is n may function electronically in $n + 1$ different

ways." Quadrivalent carbon, for example, may become $\overset{+}{\text{C}}$, $\overset{-}{\text{C}}$, $\overset{+}{\text{C}}\overset{-}{\text{C}}$, $\overset{-}{\text{C}}\overset{+}{\text{C}}$, or $\overset{+}{\text{C}}\overset{-}{\text{C}}\overset{+}{\text{C}}\overset{-}{\text{C}}$.

The conversion of a structural formula into an electronic formula by assigning positive and negative charges to opposite ends of the bonds is governed mainly by the study of ionization and electrolysis, oxidation-reduction processes, and hydrolytic reactions. The following examples show how familiar reactions are analysed. Firstly, the electrolysis of an aqueous solution of hydrochloric acid is represented by the scheme $\text{H}^+ \text{---} \text{Cl}^- \rightleftharpoons \overset{+}{\text{H}} + \bar{\text{Cl}}$, but it is further

assumed that the ion $\overset{+}{\text{H}}$ may not only lose its single positive charge at the cathode but may acquire an additional electron to become a

negative ion, $\bar{\text{H}}$. This ion is repelled from the cathode and immediately combines with an approaching positive ion to form a molecule of hydrogen. The representation is $\bar{\text{H}} + \overset{+}{\text{H}} \rightarrow \text{H}^+ \text{---} \bar{\text{H}} = \text{H}_2$.

Similarly, the negative ion, $\bar{\text{Cl}}$, may give up two electrons to the anode and become $\overset{+}{\text{Cl}}$ until it meets another $\bar{\text{Cl}}$ to form Cl_2 ; thus, $\bar{\text{Cl}} - 2\ominus \rightarrow \overset{+}{\text{Cl}}$ and $\overset{+}{\text{Cl}} + \bar{\text{Cl}} \rightarrow \text{Cl}^+ \text{---} \bar{\text{Cl}} = \text{Cl}_2$. Secondly, the

action of hydrochloric acid on zinc serves to illustrate the electronic conceptions of oxidation and reduction. Oxidation of an atom or an ion means the acquisition of positive or the loss of negative charges; conversely, reduction means the acquisition of negative or the loss of positive charges. In the above reaction, the zinc atom,

Zn, is oxidized to the zinc ion, Zn^{++} , and the hydrogen ions $2\overset{+}{\text{H}}$, are reduced to molecular hydrogen, H_2 . There is nothing novel in this conception of the close connexion between the electrical charges on, and the state of oxidation of an atom, but the suggested mechanism of the reaction is new. The zinc atom is supposed to be able to give

up both its electrons to the same hydrogen ion, and thus to produce negative hydrogen ions which then combine with positive hydrogen ions to give molecular hydrogen. Thus $\text{Zn} \rightarrow \text{Zn}^{++} + 2\ominus$; $\text{H}^{+} + 2\ominus \rightarrow \text{H}_2$; and $\text{H}^{+} + \text{H}^{-} \rightarrow \text{H}^{+} - \text{H}^{-} = \text{H}_2$.

Hence it is claimed for electronic formulæ that they give the state of oxidation of every atom in the compound. This may be further illustrated by considering the polarities of the valencies of the carbon atom in five typical compounds, viz. methane, methyl alcohol, formaldehyde, formic acid, and carbonic acid. By making hydrogen positive and oxygen negative throughout, the following electronic formulæ are obtained:

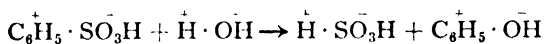


These formulæ represent the successive oxidations of the carbon atom (by the loss of electrons) in the transition between methane and carbon dioxide, and are in harmony with the fact that the slow combustion of methane produces all these compounds in the above order.

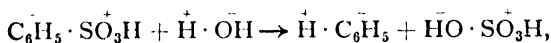
Thirdly, electronic formulæ may be assigned to substances by the study of hydrolytic reactions. The water molecule is regarded as $\text{H}^{+} - \text{O}^{-} - \text{H}^{+}$, and is a potential source of either positive hydrogen ions or negative hydroxyl ions. If the compound XY yields on hydrolysis HX and YOH, it is inferred that in the original compound the polarity of X must have been negative and the polarity

of Y positive. Therefore the reaction is written, $\text{XY} + \text{H} \cdot \text{OH} \rightarrow \text{HX} + \text{Y} \cdot \text{OH}$. If, however, hydrolysis yields HY and HOX the polarities of the radicals are reversed, and the scheme becomes $\text{XY} + \text{H} \cdot \text{OH} \rightarrow \text{HY} + \text{X} \cdot \text{OH}$. In some cases, a given compound, XY, yields on hydrolysis the four products HY, HOX, HX, and HOY.

It is then assumed that XY exists in two forms, XY and XY , which are *electronic isomers*. For example, phenylsulphonic acid, $\text{C}_6\text{H}_5 \cdot \text{SO}_3\text{H}$ hydrolyses in alkaline solution to give sulphurous acid and phenol, but in acid solution the products are sulphuric acid and benzene. The reactions are represented as



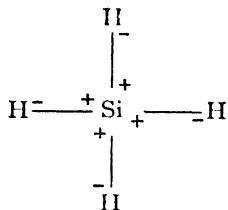
and



and indicate that phenylsulphonic acid exists as two electronic isomers or *electromers*, ($\text{C}_6\text{H}_5^+ \cdot \text{SO}_3\text{H}^- \rightleftharpoons \text{C}_6\text{H}_5^- \cdot \text{SO}_3\text{H}^+$), in tautomeric equilibrium. The same is true of hydroxylamine disulphonic acid, $\text{HN}(\text{SO}_3\text{H})_2$, which by hydrolysis in acid solution yields hydroxylamine and sulphate, and in alkaline solution nitrite and sulphite. Attempts to isolate electronic isomers, however, have failed.

Electronic amphoterism.—Hydrogen is usually represented as functioning positively, for example, in hydrochloric acid whose electronic formula is $\text{H}^+ \text{---} \text{Cl}^-$; but it may function negatively as in the metallic hydrides, for example in sodium hydride which is represented as $\text{Na}^+ \text{---} \text{H}^-$.

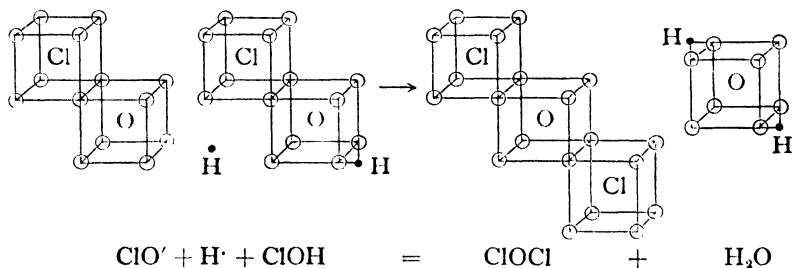
Silicon hydride reacts with caustic potash and water to give potassium silicate and hydrogen. Since the valencies of carbon in carbonic acid and carbonates are positive (p. 175), the valencies of silicon in silicates are assumed to be positive also; and since neither the caustic potash nor the water acts as a reducing agent, it is concluded that the valencies of silicon in the hydride must originally have been positive. The electronic formula of silicon hydride thus becomes



and gives an example of negative hydrogen. This example is used to justify the attachment of hydrogen to the analogous element carbon by bonds of negative polarity. It will be seen later that Fry's electronic formula for benzene shows three atoms of hydrogen functioning positively and three negatively (p. 181). Chlorine, however, is more usually represented as an electronegative element, though it is claimed that it may also act electropositively. Thus, when chlorine is dissolved in water, hydrochloric and hypochlorous acids are formed in equivalent amounts, $\text{Cl}_2 + \text{HOH} \rightleftharpoons \text{HCl} + \text{HOCl}$. In this reaction* one chlorine atom unites with the positive hydrogen

* Bassett and Durrant (*J. Chem. Soc.*, 1927, 1404) speak of the hydrolysis of sulphur and give an equation analogous to the one above, viz. $2\text{S} + 2\text{HOH} \rightleftharpoons \text{H}_2\text{S} + (\text{HO})_2\text{S}$.

ion and must therefore be negative; the other unites with the negative hydroxyl ion and must therefore be positive. The electronic equation becomes $\text{Cl}^+ \text{---} \text{Cl}^- + \text{H}^+ \text{---} \text{OH}^- \rightleftharpoons \text{H}^+ \text{---} \text{Cl}^+ + \text{Cl}^- \cdot \text{OH}^-$, and the oxidizing properties of hypochlorous acid are attributed to the instability of positive chlorine and its tendency to become negative chlorine. In this connexion it is of interest to note that Noyes and Wilson* have shown that, while HOCl has a low hydrogen ionization, and exists undissociated in solution, the gaseous phase above the solution at 25° contains the chlorine in the form of chlorine monoxide, $\text{Cl}:\text{O}:\text{Cl}$. This they say can only be explained by supposing a chlorine atom, on separating from the oxygen of the hypochlorous acid, to leave behind with the oxygen atom the two electrons forming the bond. This resulting positive chlorine atom then unites with the hypochlorite ion, $\text{Cl}:\text{O}:$, to form the chlorine monoxide. The authors cite this case as an example of the separation into positive and negative forms, of atoms which are always assumed by the explanations of the octet theory to be joined by a non-polar union, and as an example of the temporary existence of a chlorine atom with only six electrons in its outer shell. It seems, however, questionable whether the explanation given by Noyes and Wilson of the mechanism of this reaction is distinguishable from that of the octet theory, viz. that the oxygen atom of a hypochlorite ion in solution is able to share a pair of electrons with an adjacent chlorine atom of an undissociated molecule of HOCl, causing the chlorine atom immediately to abandon the two electrons previously shared in the HOCl molecule. This is shown in the following figure. It



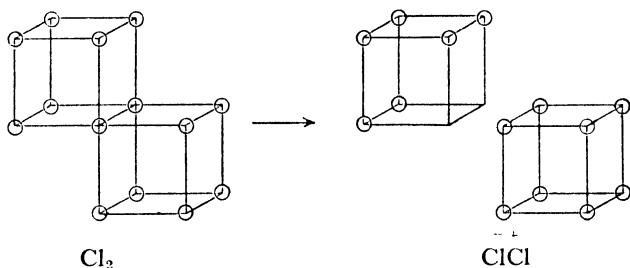
becomes a fine point to say how long the chlorine atom existed with a sextet of electrons in its outer shell. The experiments of Aston, which have demonstrated the isotopes of chlorine, are given

* Noyes and Wilson, *J. Amer. Chem. Soc.*, 1922, **44**, 1630.

by Noyes and Wilson as a further example of the existence of positive chlorine atoms; the ions in a highly evacuated discharge tube form, however, under abnormal circumstances, and their existence is transient.

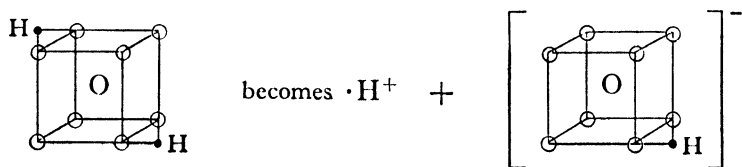
Acceptance of the positive nature of the chlorine atom in hypochlorous acid is essential to the electronic explanation of many reactions with benzene derivatives which will be discussed later (p. 182), so that it is of interest to translate the above equation into the language of the octet theory.

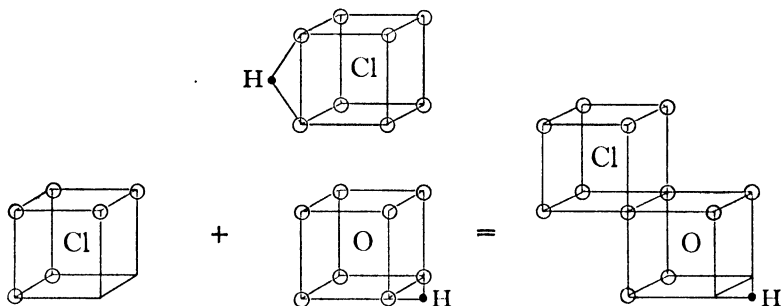
The formula $\overset{+}{\text{Cl}}\overset{-}{\text{Cl}}$ implies that the molecule of chlorine has dissociated in such a way that one of the chlorine atoms has acquired both the shared electrons thus,



Such a dissociation is not discussed by Langmuir, but Lewis has mentioned it in explanation of the conductivity of gaseous iodine. Lewis regards the above as extreme states which exist perhaps in the case of a few of the molecules, but he believes that the vast majority of them exist in a large number of intermediate conditions represented by the octets sharing one electron. The theory of Fry, however, permits of no intermediate conditions; the polarity of an atom in a compound is always represented by an integral number.

Proceeding with the reaction, the next step is that the water molecule dissociates into a hydrogen ion and a hydroxyl ion, then the negative chlorine attaches itself to the positive hydrogen, while the positive chlorine unites with the negative hydroxyl, thus:

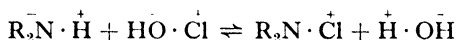




The formulation of hypochlorous acid as $\overset{+}{\text{Cl}} \cdot \overset{-}{\text{O}}\text{H}$ implies that the hydroxyl group retains full possession of the shared pair of electrons, in other words, that union as conceived by the octet theory does not take place. It is probable, therefore, that electronic formulæ are better suited to indicate how a compound will react than to represent the actual distribution of electrical charges in the molecule. The majority of chemists using electronic formulæ will agree with Noyes * that it is not necessary to believe that in the molecule of chlorine one atom is positive and the other negative, but only that in reactions the two atoms separate, one becoming positive and the other negative. Fry,† however, considers that the molecule is permanently ionized, and that measurements of molecular volumes give evidence in favour of his view.

The use of formulæ to indicate how a compound will react is a fundamental development in chemical symbolism, and is becoming more common with the application of electronic theories; structural formulæ, therefore, have the added burden of simultaneously functioning as reaction formulæ.

According to Fry, another example of positive chlorine is furnished by the chloramines, because, on hydrolysis and interaction with hydrogen iodide, the chlorine atoms are replaced by hydrogen and not by hydroxyl. Further, chloramines are prepared by the action of hypochlorous acid upon amines, thus



Other examples of atoms or radicals that show electronic amphoterism are iodine and the cyanide radical. Iodine, usually negative,

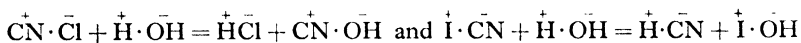
* W. A. Noyes, *Trans. Farad. Soc.*, 1923, **19**, 524. Cf. Lapworth, *J. Chem. Soc.*, 1901, 79, 1267; Noyes and Lyon, *J. Amer. Chem. Soc.*, 1901, **23**, 463; Stieglitz, *J. Amer. Chem. Soc.*, 1901, **23**, 796.

† Fry, *The Electronic Conception of Valence*, p. 183.

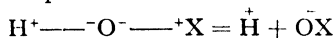
is positive in the compound ICl, as is shown by the equation representing hydrolysis,



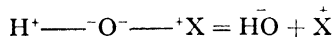
The cyanide radical is positive in chlorocyanogen because hydrolysis produces cyanic acid: it is negative in iodocyanogen because hydrolysis produces hydrocyanic acid. The equations are:



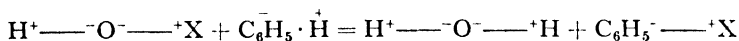
Ionic amphoterism.—The study of electronic formulæ suggests a wider occurrence of amphoterism among compounds than is usually recognized. A compound is said to be amphoteric when it may ionize in different ways so as to act either as an acid or base; the hydroxide of aluminium may be taken as a typical example. The stronger oxyacids like nitric and sulphuric acids are usually regarded not as amphoteric, but as sources of hydrogen ions which react with bases. This is shown by the equation



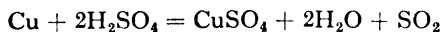
where X represents Cl, NO₂, or SO₃H. But when these acids act as chlorinating, nitrating, or sulphonating agents they appear to dissociate as bases. Thus with benzene they dissociate according to the equation



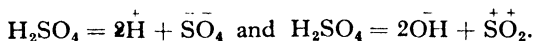
and the complete reaction is represented by



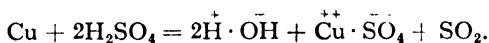
From this point of view the oxidizing properties of oxyacids depend on their ability to dissociate as bases. Another example is furnished by the action of sulphuric acid on copper:



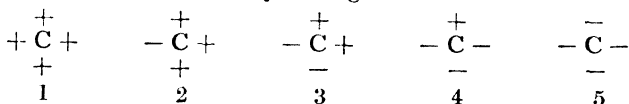
According to Fry, one molecule of H₂SO₄ gives hydrogen ions, the other hydroxyl ions which products unite to give two molecules of water:



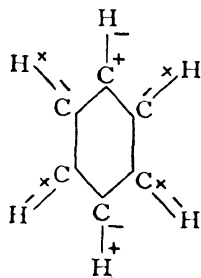
The positive ion $\overset{+}{\text{S}}\bar{\text{O}}_2^+$ is reduced to the neutral state by oxidation of Cu to $\overset{+}{\text{Cu}}$, and liberated as a gas. The complete equation becomes,



The electronic formula of benzene.—The most general space formula for benzene that has been given by the older theories of structure is due to Collie (p. 115). It supposes a system of six tetrahedral carbon atoms each united to a hydrogen atom, but free to move about its centre and the centre of gravity of the whole system. Plane projections of the possible symmetrical groups are given by Collie as shown on p. 116. The second and fourth of these are forms of the Kekulé formula, and the third is the centric formula. If these forms are mutually interchangeable, it will suffice to consider the application of Fry's electronic theory to one of them only, the centric formula. It has been shown (p. 175) that the carbon atom may function in five ways electronically, and give rise to the following types:



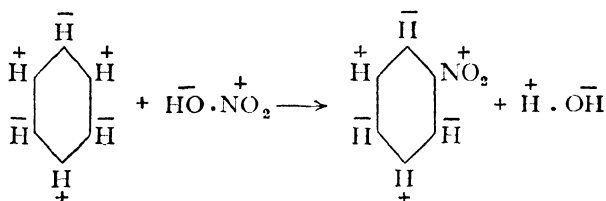
An essential part of Fry's electronic theory is that all bonds are polar, so that there must be carbon atoms of alternate polarity in the benzene ring. Introducing the various possible types of carbon atoms above by taking either six atoms of type 3, three each of types 2 and 4, or three each of types 1 and 5, three centric electronic formulæ are obtained. These need not be reproduced here as they all have one feature in common, viz. that the carbon and hydrogen atoms have alternate polarity. Thus the essentials of all three formulæ are represented by the abbreviated one shown in the accompanying figure. The novelty of Fry's formula is the appearance of three negative and three positive hydrogen atoms; and it is this feature that is most likely to prove unacceptable to the majority of chemists. It is perhaps more reasonable to suppose that the replacement of a hydrogen atom in benzene by a more or less polar substituent induces an opposite polarity in the neighbouring atom causing alternate polarities throughout the whole molecule. This is the underlying idea of Lapworth's theory of induced polarities which will be discussed later.* The substituent atom is called by Lapworth the *key atom*. Since the plus and minus signs of Fry's formula for benzene would seem to indicate intramolecular ionization in the normal state of the molecule, it is better to regard the formula as



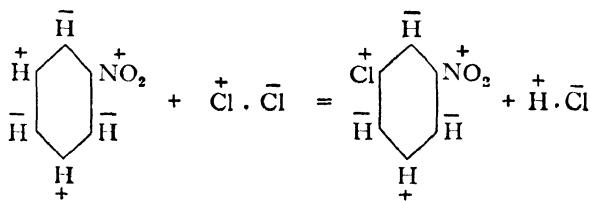
* Cf. also Flurschein's theory (p. 193).

a reaction formula which indicates how benzene behaves in reactions immediately its normal structure is disturbed. Some examples will now be given to show how the formula explains the formation of certain derivatives and not others.

Substitution in the benzene ring.—The action of nitric acid on benzene produces nitrobenzene and water; so, according to the considerations previously discussed (p. 180), nitric acid dissociates as a base furnishing a negative hydroxyl ion which combines with one of the positive hydrogen atoms of the benzene molecule to give water. Hence the NO_2 group is positive and replaces one of the positive hydrogen atoms. The scheme is shown below. Further



nitration yields meta-dinitrobenzene; this is in accordance with the electronic formula because the meta- position is positive while the ortho- and para- positions are negative. The fact that chlorination of nitrobenzene produces only meta-chloronitrobenzene indicates the substituting chlorine atom is positive also. The reaction is



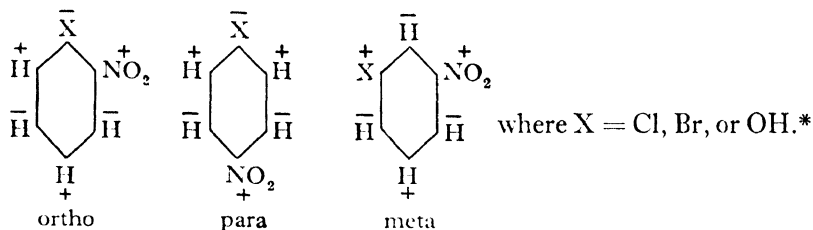
The fact that nitration of chlorobenzene produces ortho- and para-chloronitrobenzene but not the meta- derivative must now be explained. It indicates that the chlorine atom in chlorobenzene is

negative, thus $\begin{array}{c} \bar{\text{Cl}} \\ + \text{H} \diagup \quad \diagdown \text{H}^+ \\ | \quad \quad | \\ \bar{\text{H}} \quad \quad \text{H}^+ \\ | \\ \text{H}^+ \end{array}$, so that nitration results in NO_2^+ groups

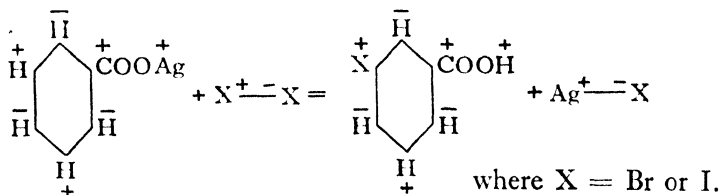
replacing the $\overset{+}{\text{H}}$ atoms, which atoms occur only in the ortho- and para-positions.

Knowledge of the polarity of a chlorine atom would appear to have little consequence were it not found to provide ready explanations of the behaviour of the compound containing it. We find, however, that it does explain the apparently anomalous behaviour of ortho-, para-, and meta-chloronitrobenzenes when these are heated with alcoholic solutions of potassium hydroxide, whereas the ordinary structural formula does not. The experimental facts are that KOH produces complete hydrolysis with the ortho- and para- compounds but not with the meta-. According to the electronic theory, the hydroxyl group is negative and can therefore replace only negative chlorine atoms. These occur, according to the theory, in ortho- and para-chloronitrobenzenes, but not in the meta- compound; and it is the ortho- and para- compounds which are hydrolysed by alkali, whilst the meta- compound is unchanged by this treatment. Thus the electropolarity theory is supported.

The bromo- and the hydroxy-nitrobenzenes behave similarly to the chloronitrobenzenes, so that the general formulæ for these compounds may be written



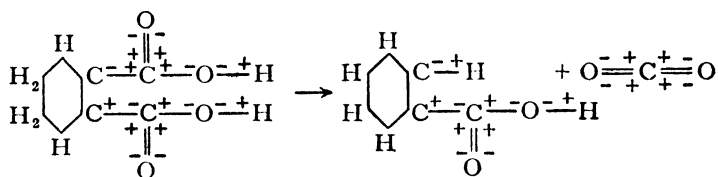
Another example illustrating the application of Fry's electronic theory to substitution in the benzene nucleus is provided by the action of the halogens upon silver benzoate. It is found that bromine and iodine produce meta-bromo- and meta-iodobenzoic acids respectively. The equation for the reaction is given as:



* Fry finds it convenient to place the negative atom or group at the top of the formula; this accounts for the unusual appearance of the meta- compound.

The electronic formula for silver benzoate shows the carboxyl radical to be positive because the compound is a derivative of carbonic acid in which all the valencies of carbon are positive (p. 175); the halogen molecule dissociates into a negative atom, which combines with the positive silver atom, and a positive atom which must replace a positive atom in the ring, i.e. the halogen atom must occupy a position in the ring that is meta- to the carboxyl atom.

It may be noted that the carboxyl radical is not always positive. Thus, in phthalic acid, where there are two carboxyl groups occupying positions that are ortho- to each other, they could be both considered positive only by sacrificing the alternate polarities of the carbon atoms of the benzene ring. This sacrifice, however, is never made; the two carboxyl groups in phthalic acid are assumed to have opposite polarity. In confirmation of this, experiment shows that oxidation of dihydrophthalic acid produces equivalent amounts of benzoic acid and carbon dioxide.* The fact that benzene and double the quantity of carbon dioxide are not produced indicates a difference between the two carboxyl groups which is not explained by any graphic formula. If, however, one of the carboxyl groups of dihydrophthalic acid be considered positive, and therefore in a stage of oxidation corresponding to that of carbonic acid (p. 175), and the other carboxyl group negative corresponding to the stage of oxidation of the carbon atom in formic acid, which does not lose carbon dioxide, then the reason why the acid yields one molecule only of carbon dioxide becomes clear. The reaction is shown thus:



Apparently no experimental evidence is available to prove that the benzoic acid with a negative carboxyl group so produced can be distinguished from the ordinary benzoic acid with a positive carboxyl group. If two electronic isomers exist, it must be assumed further that they are readily convertible, one into the other. There is no difficulty in abstracting two molecules of carbon dioxide from *phthalic* acid by the use of soda lime. An explanation of this, consistent with that above, involves the assumption that the reaction

* Baeyer, *Ann.*, 1892, 269, 178.

occurs in two stages, benzoic acid with a positive carboxyl group being first produced, which undergoes intramolecular ionization before the second molecule of carbon dioxide is lost.

The Crum Brown and Gibson rule.—The electronic theory provides a simple explanation of the Crum Brown and Gibson rule. This rule refers to the conversion of a monobenzene derivative, C_6H_5X , into a dibenzene derivative, C_6H_4XY , whereby either a meta- compound or a mixture of ortho- and para- compounds is produced. The criterion determining which alternative occurs is the possibility or impossibility of the *direct* oxidation of HX into HOX ; if the direct oxidation is possible the meta- compound is formed, if impossible, a mixture of the ortho- and para- compounds is formed. No explanation has hitherto been suggested for the operation of the rule, but it is found to be of general application. From the electronic point of view, however, the explanation depends on the difference of polarity of X in the compounds HX and HOX . It has already been pointed out (p. 180) that X functions negatively in HX but positively in XOH so that the electronic rendering of the Brown and Gibson rule becomes: When X in C_6H_5X is negative and the entering substituent Y is positive, then ortho- and para- di-derivatives result; when X in C_6H_5X is positive and the entering substituent Y is positive, then meta- di-derivatives are formed. On p. 182 examples of this rule were discussed in the nitration of chlorobenzene, and in the chlorination of nitrobenzene.

Frequently substitution reactions produce isomeric ortho-, para-, and meta- di-substituted derivatives simultaneously. The Brown and Gibson rule does not apply to these cases. The reactions are interpreted on the electronic theory as evidence of the existence of the electronic isomers $C_6H_5\overset{+}{X} \rightleftharpoons C_6H_5\overset{-}{X}$ in dynamic equilibrium.

For example, the nitration of toluene produces 56 per cent of the ortho-, 40.9 per cent of the para-, and 3.1 per cent of the meta-nitrotoluene. The nitro group in nitric acid must be positive according to Fry's scheme, $\overset{-}{H}\overset{+}{O} \cdot \overset{+}{N}O_2$ (p. 182), and must therefore replace a positive hydrogen atom. This occurs in the ortho- and para- positions relative to the CH_3 group in 96.9 per cent of the total, indicating that the CH_3 group is negative (since polarities are alternate in the benzene ring), but occurs in the positions meta- to the CH_3 group in 3.1 per cent of the total indicating that positive CH_3 groups are also present. It may be mentioned, however, that it is more usual on other theories to regard the nitro group as invariably negative

and the methyl group as positive. Assuming alternate polarities of the carbon atoms in the ring, these theories explain equally well the formation of the ortho- and para- compounds; they cannot explain the meta- compound without assuming (as Fry does) that the methyl and the nitro groups exist in small quantities with similar polarities.

MODERN DUALISTIC THEORIES

Intramolecular Ionization.—In the preceding chapter, a lengthy quotation from one of Sir J. J. Thomson's Silliman Lectures has been given in which, for the first time, the application of the electron in chemistry was discussed. The part played by the electron in chemical change has since been realized to be fundamental. Originally it was supposed that all chemical action was due to the transference of electrons from one atom to another. This implies an electrochemical dualism which when consistently applied to all compounds is the rock on which the theory of Berzelius foundered. The assumption that every atom in the normal state of a compound is charged through the gain or loss of an integral number of electrons is generally regarded as too extreme a view, because, not only is it difficult to believe that the constituent atoms of the larger molecules of organic compounds can be held together by an assemblage of ions, but the picture which we can now form of the molecule—thanks to the progress made in the knowledge of atomic structure—makes it unlikely that the normal state of all molecules is one where neighbouring atoms can lie side by side, one possessing an excess and the other a deficiency of electrons. The difficulties of the dualistic theory have been overcome by Lewis, as already noted (p. 164), by postulating the sharing of electrons by atoms.

When two atoms share equally a pair of electrons, a molecule of the other extreme type is formed, viz. a non-polar molecule, or one in which the constituents are electrically neutral.

Probably the majority of compounds have molecules which lie between these two extremes. Even in the same compound all molecules are not to be regarded as in the same state; at a given instant, some are more polar than others.

It is probable, however, that chemical reaction occurs only between molecules that are more or less polarized. It is common to find reactions between molecules occurring only in presence of a third substance, which is called a catalyst. The function of a catalyst

may therefore be to convert non-polar molecules into more polar states. Complete ionization need not be assumed; it may be necessary only to loosen the existing bond, an operation which in the final sense may be regarded as the opening out of the lines of force which constitute the chemical bond. Other agencies not usually called catalysts may promote chemical action, for example, a particular solvent, or the material of the vessel containing the reactants. It has been found* that ethylene reacts with bromine for the most part, if not entirely, on the walls of the containing vessel, and that there is no evidence of gaseous reaction. This has been confirmed by Norrish,† who showed that a carefully dried mixture of pure bromine and ethylene reacted rapidly when placed in a glass vessel at 0° C., but hardly at all when placed in a paraffin-wax coated vessel.

The view is becoming more generally held that all chemical reactions, among organic substances as well as inorganic, are preceded by ionization.‡

When a molecule of a substance adopts a more or less polar form, through one of its constituents obtaining at the expense of the other constituent or constituents a greater share of the available electrons than that required to maintain its electrical neutrality, the substance is said to be intramolecularly ionized. The term does not necessarily imply complete transferences of electrons, because the charges on the atoms are usually fractional and cannot be represented always by an integral number. When, however, the molecule is destroyed, through taking part in a chemical reaction, it is necessary to assume either complete ionization or none at all between the parts of the molecule which are separated, since the electron is indivisible.

Viewing this whole subject from the standpoint of the symbolic representation of the molecule, which is the special concern of this book, the question arises, Is it possible to have a simple system of symbols that will represent the molecule in its normal state, indicating the correct strength of attachment between all the atoms throughout the molecule, and, at the same time, show how the molecule will react to different reagents? In view of what has been discussed above regarding the varying polarity of different molecules of the same substance, it seems difficult enough to represent ad-

* Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, **45**, 1014.

† Norrish, *Trans. Faraday Soc.*, 1923, **19**, 520.

‡ Cf. Lowry, *Trans. Faraday Soc.*, 1923, **19**, 491; Rideal, *ibid.*, p. 514 *et seq.*; Lewis, *Valence and the Structure of Atoms and Molecules*, p. 133.

quately the molecule in its normal state, but the fact remains that different authors have, during the last decade, used symbols, chiefly plus and minus signs, dots, and arrows, added to the symbols of the elements, which are intended to be both structural formulæ and reaction formulæ; but the uses and implications of these symbols have not been standardized.

One system which correlates the symbols of Thiele's partial valencies with those of Lewis, Langmuir, and Thomson will now be discussed. The single bond corresponds with the sharing of two electrons, and is represented by the horizontal line, or by the colon; thus, H_2S is represented by $\text{H}-\text{S}-\text{H}$, or $\text{H}:\text{S}:\text{H}$. Each dot represents one electron. It may be desirable to show the complete octet, thus, $\text{H}:\ddot{\text{S}}:\text{H}$. In one way this formula is more suggestive than the formula $\text{H}-\text{S}-\text{H}$, because it shows that the central sulphur atom has two latent valencies that can be utilized by appropriate atoms. Since the sulphur atom has already a completed octet, it can combine only with atoms of elements which will share pairs of electrons with it without contributing any; for example, in the

$$\begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}:\ddot{\text{S}}:\ddot{\text{O}}: \\ :\ddot{\text{O}}: \end{array}$$

sulphate ion : two of the oxygen atoms cannot have contributed to the pairs that they share with the central atom.

The double bond is represented by four dots, for example,

$$\begin{array}{c} \text{H} \quad \text{H} \\ \ddot{\text{C}}::\ddot{\text{C}} \end{array}$$

ethylene is represented as $\text{H}:\ddot{\text{C}}::\ddot{\text{C}}:\text{H}$. It has already been pointed out that the reactivity of ethylene has been taken by Lewis to indicate that a proportion of the molecules may be repre-

$$\begin{array}{c} \text{H} \quad \text{H} \\ \ddot{\text{C}}::\ddot{\text{C}} \end{array}$$

sented by the formula $\text{H}:\ddot{\text{C}}::\ddot{\text{C}}:\text{H}$. This is equivalent to the partial

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \vdots \quad \vdots \end{array}$$

valency formula showing that the dotted line intro-

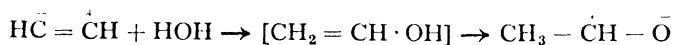
duced by Thiele, to represent a partial valency, can be regarded as equivalent to the dot which represents an electron, and therefore half a normal valency. Lowry,* however, has suggested that carbon

* *Jour. Chem. Soc.*, 1923, 123, 822.

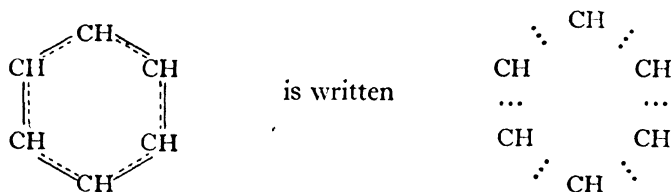
atoms linked by a double bond usually react as though that bond contained one covalency and one electrovalency, that is, the double bond breaks unsymmetrically so as to leave eight electrons on one atom and six on the other. Such a bond he calls a "mixed double bond" or "semipolar double bond". Ethylene would be represented

(immediately prior to its disruption) as $\text{H} : \ddot{\text{C}} : \ddot{\text{C}} : \text{H}$, $\overset{+}{\text{CH}}_2 - \overset{-}{\text{CH}}_2$, or $\text{CH}_2 \rightleftharpoons \text{CH}_2$, the barb in the last formula being used by Lowry to indicate the transference of an electron from one carbon atom to the other. Such an unsymmetrical break is entirely analogous to Lewis's view of the dissociation of the diatomic molecule of iodine into an octet and a sextet, which has been discussed on p. 161.*

Lowry further suggests that the triple bond may be "mixed", and has represented acetylene with a double bond and an electrovalency, thus, $\text{H} : \text{C} :: \ddot{\text{C}} : \text{H}$, or $\overset{+}{\text{CH}} = \overset{-}{\text{CH}}$, or $\text{CH} \equiv \text{CH}$. The hydrolysis of acetylene to acetaldehyde is then represented by the equation

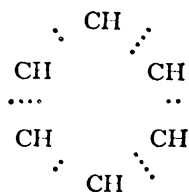


The subdivision of valency.—It has long been felt that the facts of organic chemistry can best be explained by assuming the divisibility of the normal valency. The terms partial valency and residual valency are not new. Thiele assumed the divisibility of the normal valency into two partial valencies, and the divisibility of the double bond into a partial valency and a single bond plus a partial valency. The notation employed, viz. =, —, —, · ·, implies electrons to the number of four, three, two, and one, respectively held in common by two atoms, and may be replaced by the corresponding number of dots. Thus, the symmetrical partial valency formula for benzene,

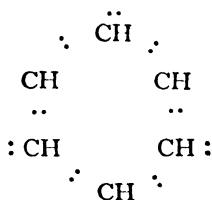


* Substances which are intramolecularly ionized, according to Sir J. J. Thomson's measurements, form double molecules in the liquid state. Walker (*Trans. Faraday Soc.*, 1923, **19**, 521) has found that liquid ethylene is not associated at all, in accordance with the view (p. 187) that, under normal conditions, ethylene exists in a non-reactive form. Lowry's formula, therefore, does not represent ethylene in its normal state (*vide loc. cit.*, pp. 490-1).

It corresponds with Sir J. J. Thomson's formula given on p. 158
The Kekulé formula would be

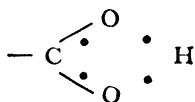


and differs from the preceding one by a relatively insignificant rearrangement of electrons. The difference is due solely to the movement of three electrons, not even from atom to atom, but merely to new positions in the octets in which they were originally stationed. There have been discussed so far in this book about twenty different graphic formulæ for benzene. The variety of symbolic representation suggests wide differences in the manner in which the atoms of benzene are linked together, but it is interesting to note how little these linkages do differ when they are interpreted in terms of the positions of electrons. Perhaps the most distinctive of those considered is that of Fry, where the carbon atoms have alternate polarities, equivalent to an excess and a deficiency of an electron alternately. Adopting the above notation, Fry's formula becomes



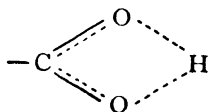
So that carbon atoms possess octets and sextets alternately.

Kermack and Robinson* have suggested that a simple and convenient notation would be to represent the single electron by a dot, and two electrons by an ordinary bond. The formula for the carboxyl group would then be



* *J. Chem. Soc.*, 1922, 121, 437.

corresponding with the expression

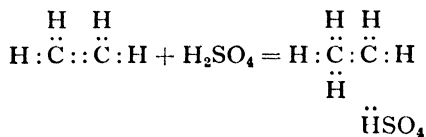
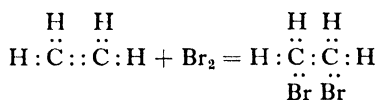


recommended by Hantzsch, and by Lapworth.

These authors have suggested that the facts of chemistry are best interpreted by assuming that contiguous atoms can share one or three electrons as well as two and four. In the course of their paper they give several examples, of which the above formula for the carboxyl group is one.

It will be noted, however, that it has long been the practice to indicate the ordinary bond by a dot, the reason being, probably, to economize space. Thus it is common to find acetic acid as $\text{CH}_3 \cdot \text{COOH}$, or $\text{CH}_3 \cdot \text{COOH}$; in the first of these, the lower position of the dot seems to show that its use is to emphasize that methyl is a radical, whereas in the second formula the dot indicates a bond. Similarly, it is common to find that the colon is used to represent the double bond, thus allyl alcohol is written $\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{OH}$. Confusion is thus likely to arise from ambiguous use of dots.

The question next arises: Can a normal valency be subdivided into more than two partial valencies? At first sight the answer seems to be, No, unless one electron can be shared by more than two atoms. If, however, the valency bond is regarded as composed of a bundle of lines of force, it does not seem unlikely that these lines may be distributed over three or even more than three atoms. At any rate, it seems improbable that the normal valency, when subdivided into two partial valencies, is always divided equally. If a double bond is broken so as to give rise to a single bond and two partial valencies, it is unlikely that these partial valencies will be always exactly equal; it will depend on the nature or "electron demand" of the reagent which breaks the double bond. For example,



the addition of two bromine atoms to the molecule of ethylene would probably rupture the double bond so as to give initially two equal partial valencies, but the molecule of sulphuric acid, adding in a similar way to the molecule of ethylene, would probably not break the double bond equally, and the resultant ethylsulphuric acid would be to a certain extent intramolecularly ionized. This is what is meant by Lewis when he states that ethylene exists in a form intermediate between the forms represented by the two formulæ on p. 188. The extreme case where one valency of the double bond between the two atoms is appropriated entirely by one of the atoms, gives rise to the "mixed double bond" of Lowry already discussed (p. 189).

The loose form of attachment between solute and solvent may be another example of the operation of valencies which in magnitude are only small fractional parts of a normal valency.

The nature of partial valency has been described in a general way by Sir Oliver Lodge as follows: * "On any view electrons are supposed to repel and be attracted with a force varying as the inverse square of the distance, and this is only consistent with a very large number of lines of force radiating from each and starting out in every direction equally.

"When opposite charges have paired off in solitude, every one of these lines starts from one and terminates on the other constituent of the pair, and the bundle or field of lines constitutes a full chemical bond; but bring other charges or other pairs in the neighbourhood, and a few threads or feelers are at once available for partial adhesion in cross directions also."

It would thus appear that not only is the strength of a valency bond variable and dependent on its environment, but also that the direction of the bond is variable and dependent on its environment. The variability of strength and localization of bonds is closely connected with the electrical nature of chemical affinity; and it may be said that covalency represents the extreme type of localized bond of maximum strength, and electrovalency the extreme type of non-localized bond of minimum strength.

Werner, in his study of co-ordinated compounds, concluded that valency was not localized, and, in consequence, he did not accept van't Hoff's tetrahedral model of the atom. The origin of the controversy regarding localization and non-localization of bonds can be traced to the same factors that gave rise to the controversy between

* *Nature*, 1904, 70, 176.

the unitary theory of Dumas and the dualistic theory of Berzelius. Just as the unitary theory finds its greatest support in the facts of organic chemistry, so does the theory of the localization of bonds. The theory of Lewis which reconciled those of Dumas and Berzelius serves also to reconcile the views of Werner and van't Hoff on the localization of bonds. The majority of compounds are linked together by bonds which are intermediate between the covalent bond (the exactly equal sharing of a pair of electrons) and the electrovalent bond (due to the entire appropriation of the shared pair by one of the atoms); the more nearly the bond is covalent, the more localized it is, but the more polar the atoms become, the more diffused is their affinity.

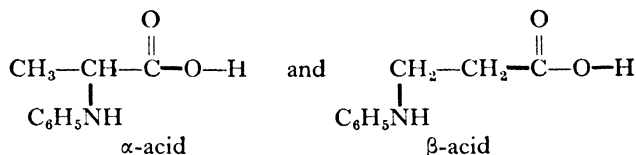
This idea of the variability of the affinity content in bonds was also held by Werner and by Claus. The introduction of a substituent in a molecule was considered to influence the strength of the linkages throughout the molecule. The compounds formed by chains of carbon atoms are uniquely suited for the study of such an effect, and, in consequence, a large number of theories, hypotheses, and rules have been put forward dealing with it. It is probable that in this field symbols have been used with least precision, and with greatest variety of meaning by different authors.

The first hypothesis that a substituent may cause the distribution of chemical force to alternate over a chain of atoms was put forward by Flürscheim in 1902. The essential idea was that "if an atom, such as tervalent nitrogen, with more available residual affinity than hydrogen, is linked, for instance, to a carbon atom in benzene, it makes a greater demand than would hydrogen, on the affinity force of this carbon atom. The equilibrium of forces which existed in benzene is thereby disturbed, because carbon 1 has now less affinity left to bind carbons 2. These now have more unbound affinity available than they had in unsubstituted benzene, and since there must be an equilibrium between free and bound forces, the free affinity at carbons 2 and the bound affinity between carbons 2 and 3 become greater than in benzene, and so on. It is therefore to carbons 2 and 4 that a reacting molecule is attracted, forming first an intermediate (Kekulé) molecular addition product, which then changes to a substitution derivative with the new substituent in 2 or 4. If an atom, such as pentavalent nitrogen, disposes of less available residual affinity than hydrogen, the reverse process occurs, with substitution in 3."*

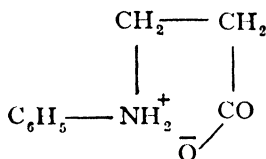
* Flürscheim, *Trans. Faraday Soc.*, 1923, **19**, 531.

Flürscheim does not base his hypothesis on any assumptions concerning the ultimate nature of chemical affinity itself; he prefers to leave that question open, and uses the broad term "affinity" without associating it with electrons. The alternation throughout a chain of atoms caused by a substituting atom is one of affinity, not one of polarity.

Flürscheim uses symbols to denote the varying amount of affinity throughout the molecule; when substitution has taken place, thick lines denote an increased amount of bound affinity, compared with the corresponding bond in the unsubstituted compound, whereas thin lines denote the reverse. For example, the substitution of the $\text{NH} \cdot \text{C}_6\text{H}_5$ group, which "has a greater affinity demand than hydrogen", in propionic acid gives rise to



The α -acid holds its ionizable hydrogen less strongly than propionic acid does, and will therefore dissociate more readily. The reverse holds for the β -acid. This is borne out by the experimental data for the dissociation constants of these acids, which show that α -anilino-propionic acid (3.8×10^{-5}) is stronger than propionic acid (1.4×10^{-5}), whereas β -anilino-propionic acid (0.4×10^{-5}) is weaker. Lowry * has suggested that the anomalous behaviour of these acids is due to the formation, in the case of β -anilino-propionic acid, of an inner salt with a 5-atom ring,



but this view has been contested by Flürscheim.†

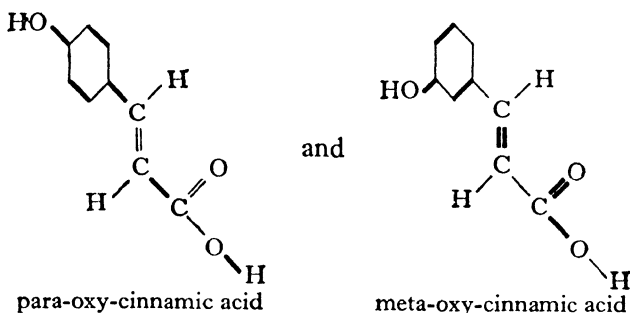
Flürscheim claims that the alternating increase and decrease of the strength of an acid by introducing a substituent occurs even when the substituting and the ionizing groups are far apart. He gives an example ‡ which cannot be explained by the formation of

* Lowry, *Trans. Faraday Soc.*, 1923, **19**, 502.

† *Loc. cit.*, p. 534.

‡ Flürscheim, *Trans. Faraday Soc.*, 1924, **20**, 17.

an inner salt, viz. that of meta-oxy-cinnamic acid and para-oxy-cinnamic acid, the former being stronger than, and the latter weaker than cinnamic acid. These acids are formulated thus:



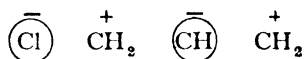
Another hypothesis based on the variation of the affinities of carbon atoms in a chain was put forward by Lapworth in 1901. It was suggested that a migration of the point or condition of free valency occurred owing to a "dissociation akin to ionization". A generalization, called the " $\alpha\gamma$ rule", was observed which expressed the fact that alternate atoms in a carbon chain act as the seats of ionic reactivity. With the advent of electronic ideas of valency this rule was phrased as indicating alternate "polarities" in the chain. Lapworth did not consider that migration of whole free valencies occurred—in other words, he did not assume a complete transference of an electron to occur from one carbon atom to another—but he postulated the migration of "partial" valencies.

In adopting his theory to modern electronic views, Lapworth* has introduced the symbols + and - into his formulæ. These symbols do not indicate the complete ionization in the molecule that the same symbols indicate when used by Fry as already described. Nor are they applied by Lapworth in such a general way as Fry applies them to explain all chemical reactions. According to Lapworth, the alternate polarity in a carbon chain does not exist in a hydrocarbon, but is induced by the introduction of an atom of polar type, called the "key atom". Hence his principle is known as "The Theory of Induced Alternate Polarities in a Chain of Atoms". The theory has been adopted and explained by Kermack and Robinson,† and the following example shows the way in which the symbols are employed. The formula $\ddot{A}:\ddot{B}:\ddot{C}:\ddot{D}$ shows a symmetrical

* *Mem. Manchester Phil. Soc.*, 1920, **64**, 1; *J. Chem. Soc.*, 1922, **121**, 416.

† *J. Chem. Soc.*, 1922, **121**, 427.

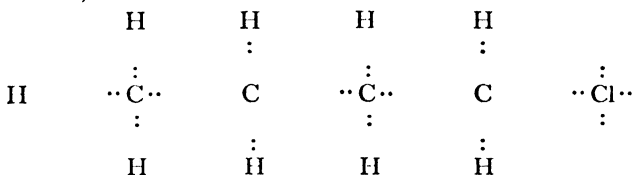
system, each atom being surrounded by an octet of electrons. If, however, the atom A is more electronegative than the others, it will tend to appropriate the two electrons shared with atom B. This will make the octet surrounding atom B unstable, and this atom will tend, not to acquire electrons from elsewhere, but to disintegrate still further. The atom C will thus obtain a greater share of the pair of electrons forming its bond with B, and tend to form a stable octet by the aid of two electrons from D. The atoms will thus be respectively, $-$, $+$, $-$, $+$. Allyl chloride furnishes an example, and would be formulated



Lapworth and Robinson apply their theory to explain the peculiarities of orientation, &c.

Højendahl,* discussing induced alternate polarities in a carbon chain on the basis of Bohr's theory, has suggested that a dot be used to represent the mean or average position of the electron during a complete revolution of its orbit. The ordinary bond is represented by two dots placed horizontally, thus $\text{C} \cdot \cdot \text{C}$. This method of formulating a bond is preferable to that of Lewis and Kermack and Robinson, because it is less likely to become confused with the symbol $\text{C} : \text{C}$ which has long been used to indicate a double bond.

Højendahl represents the double bond thus $\text{C} : : \text{C}$, and alternate polarities by placing the dots nearer in the case of negative atoms and farther in the case of positive atoms. For example, butyl chloride is shown thus,



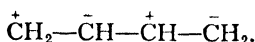
Lowry † has expressed the view that alternate polarities are characteristic of conjugated systems, i.e. of systems containing the group $\text{C}=\text{C}-\text{C}=\text{C}$, and are not developed in chains of single bonds. Lapworth and Robinson ‡ believe, however, that such a limitation of their theory is quite contrary to the facts of organic chemistry.

* Højendahl, *Jour. Chem. Soc.*, 1924, **125**, 1386.

† *Trans. Faraday Soc.*, 1923, **19**, 502.

‡ *Loc. cit.*, pp. 503 *et seq.*

Lowry* claims that his formulæ introduce a uniform nomenclature to express phenomena which cannot be represented satisfactorily by Kekulé's non-polar or covalent bond. In a conjugated system the distinction between single and double bonds disappears completely. Thus butadiene is formulated



A consequence of Lowry's suggestion is that + and - signs are used only to represent polarities caused by the complete transference of an electron, so that on every occasion that the sign + - is written, a bond - must be deleted from the conventional formula. The use of the sign + - replaces, according to Lowry, the zigzag single and double bonds of von Baeyer, the dotted lines and parentheses of Thiele, the brackets of Hantzsch, the principal and supplementary valencies of Werner, the centric bonds of Armstrong and von Baeyer, and the para-bond of Dewar's formula for benzene, all of which represent electrovalencies.

Uniformity in nomenclature is not likely to be attained in this way, however, because organic chemists dealing with this subject have not yet decided how many types of valency they require; or rather, because chemists desire to use fractional valencies to facilitate their own thoughts, and to convey their exact meaning.† Lowry's suggestions meet their requirements only to a limited extent, because his theory deals with the composite nature of double and triple bonds only, and even then he analyses these into integral portions.

It is unfortunate that the development of theories of valency has not been accompanied by an expansion in symbolism adequate to express without ambiguity the large number of ideas that exist concerning the bonds that unite atoms together in a molecule. The horizontal line, the dot, and the plus and minus signs have borne too big a burden in the development, and have a variety of meanings; so that the general chemical reader when seeing these symbols must inquire into the particular meanings assigned to them by the author of the publication he is reading. The effort required by the reader to understand the symbolism threatens to endanger his interest in the subject. A new symbol which, if generally adopted, would go far to lessen the present ambiguities, is discussed on p. 207.

* *Loc. cit.*, p. 490.

† Cf. Robinson, *Trans. Faraday Soc.*, 1923, 18, 297; Ingold, *Ann. Rep. Chem. Soc.*, 1926, 35.

FURTHER EXAMPLES OF LOWRY'S USE OF ELECTRONIC FORMULÆ

Crossed polarities.—One consequence of Lowry's view of the polarity of the double bond is that certain compounds previously thought to be conjugated are no longer considered by him to be so. These compounds contain two double bonds placed so that intermediate atoms tend to be charged positively and negatively simultaneously. This gives rise to what Lowry terms *crossed polarities*. For example, maleic acid, chosen by Thiele as a typical illustration of conjugation, is formulated $\bar{\text{O}}-\overset{+}{\text{C}}(\text{OH})-\overset{+}{\text{CH}}-\overset{-}{\text{CH}}-\overset{+}{\text{C}}(\text{OH})-\bar{\text{O}}$. The crossed polarities destroy the conjugation of the system, because, according to Lowry, it is a criterion of a conjugated system to possess, in its reactive form, an unbroken series of positive and negative charges on alternate atoms.*

Lewis † discusses the conjugation between the two carboxyl groups of maleic acid, and accounts for the difference in strength between this acid and fumaric acid by postulating an opportunity for spatial approach of the two carboxyl groups of maleic acid which is absent in the case of fumaric acid.

The Carboxyl Group.—The usual formula applied to an organic

acid, $\text{R}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$ indicates the existence of a double bond between

a carbon and an oxygen atom. Much evidence, however, goes to show that this is not a typical carbonyl union, and many formulæ have been proposed to indicate that the hydrogen atom is symmetrically situated with reference to the two oxygen atoms. Two of these have already been discussed (p. 190). Sir James Walker ‡ has

suggested the formula $=\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \text{H}$, where each bond represents a tube of force, and therefore half an ordinary unit of valency. Lowry § applies his theory of mixed double bonds, and obtains the formula

$-\overset{+}{\text{C}} \begin{array}{l} \nearrow \bar{\text{O}} \\ \searrow \bar{\text{O}} \end{array} \text{H}^+$. The significance of the dotted lines is not clear

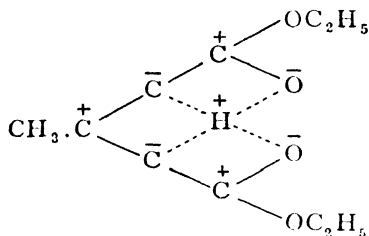
* Cf. Henstock, *Trans. Faraday Soc.*, 1923, **19**, 510.

† *Valence and the Structure of Atoms and Molecules*, pp. 144 and 155.

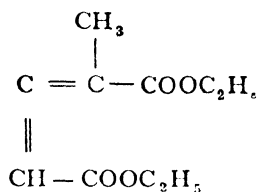
‡ Walker, *J. Chem. Soc.*, 1923, **123**, 945.

§ Lowry, *J. Chem. Soc.* 1923, **123**, 827; *Trans. Faraday Soc.*, 1923, **19**, 493.

because there is no covalency between the hydrogen atom and the oxygen atoms; the hydrogen atom is held by electrostatic forces in a position symmetrical in regard to the two negatively charged oxygen atoms; indeed it is represented as occupying a co-ordinated position, a further illustration being furnished by ethyldenemaleic ester where the co-ordination is fourfold,

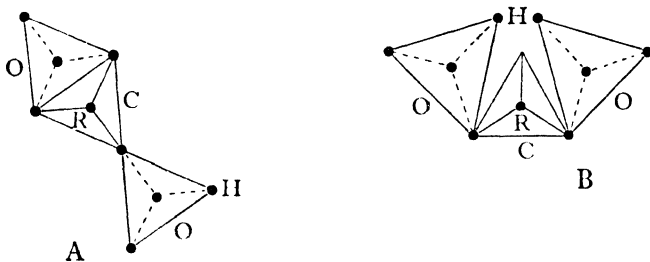


Ethyldenemaleic ester.



Usual Formula.

Huggins,* by considering the arrangement of atoms in space, arrives at the conclusion, somewhat similar to Lowry's, that the distinction between the single and the double bond has been destroyed. His model of the carboxyl group, like that of Lowry's, shows the hydrogen atom symmetrically disposed about the two oxygen atoms. It is shown in the accompanying figures as an example of the conjugation of the carboxyl group.

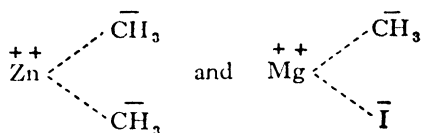


Conjugation of the Carboxyl Group.

Each black disc represents a pair of electrons; in A there is a double bond between the carbon atom and one of the oxygen atoms shown by the two tetrahedra sharing a common edge, but in B there is no double bond. Lewis supports Huggins's view, and draws attention to the ease with which two carboxyl groups conjugate, as for example in the association of acetic acid molecules which persists even to a large extent in the gaseous state.

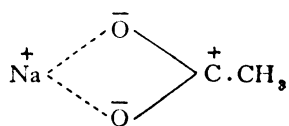
* Huggins, *Science*, 1922, 40, 679.

Polar Organic Molecules.—In addition to compounds containing ionizable hydrogen or halogen atoms three other classes of organic compounds are considered by Lowry* to be permanently polar. These are: (1) the organo-metallic compounds such as zinc methyl and the Grignard reagent, which are represented respectively as

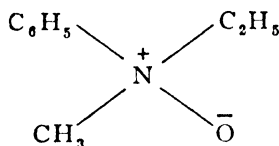


The dotted line apparently represents electrostatic forces holding the metallic cation to the two anions, and should not be confused with its usual meaning of a partial valency.

(2) Metallic salts, such as sodium ethoxide, $\text{Na}^+ \text{O}^- \cdot \text{C}_2\text{H}_5$ and sodium acetate,



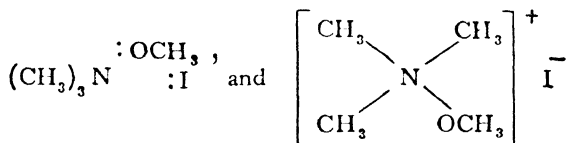
(3) Compounds containing quinquivalent nitrogen. The octet theory imposes a limitation of four covalencies for the lighter elements since each covalency requires two electrons, and in the lighter elements there are only eight electrons available. The nitrogen atom in an ammonium salt is therefore represented with four covalencies and one electrovalency, for example $\text{NH}_4^+ \text{Cl}^-$, and the compound is permanently polar. In the case of methylethylaniline oxide,



the limitation of the covalencies to four indicates that the nitrogen atom has only one covalent bond available for the oxygen atom, and that the molecule is permanently polar as shown in the formula.

* Lowry, *loc. cit.*

The same meaning is attached by L. W. Jones * to his formula for trimethylamine oxide, $(\text{CH}_3)_3\text{N}:\text{O}$, although the symbols used are different. The position of the colons, which are used to represent pairs of electrons, is intended to indicate that one pair clings to the nitrogen atom and the other to the oxygen atom in the reactions of the compound.† The addition of methyl iodide to this compound gives trimethylmethoxyammonium iodide which would be equally well represented by the formulæ



which have the same meaning.

The parachor.—In view of the wide speculation concerning the nature of the bonds that link atoms together in chemical compounds, and the differences of opinion that exist regarding the mechanism and number of varieties of these linkages, any direct experimental evidence that can be brought to bear on the subject is particularly welcome. It has been shown by Sugden‡ that such direct evidence is available from measurements of the surface tensions and densities of substances. Sugden uses a relationship between surface tension and density discovered by Macleod,§ viz.

$$\gamma = C(D - d)^4$$

where γ is the surface tension, and D and d the densities of liquid and vapour respectively, all at one temperature, while C is a constant which for non-associated substances is independent of the temperature.

Multiplying the fourth root of Macleod's constant by the molecular weight, M , Sugden obtains the expression

$$P = \frac{M}{D - d} \gamma^{\frac{1}{4}}.$$

The quantity $M/\overline{D - d}$ has the dimensions of volume; at low temperatures, where d is negligible compared with D , it is actually the

* Jones, *J. Amer. Chem. Soc.*, 1914, **36**, 1284.

† The properties of the amine oxides have been discussed in terms of the electronic theory in an interesting and suggestive way by Lewis in his book on Valence.

‡ Sugden, *J. Chem. Soc.*, 1924, **125**, 1177.

§ Macleod, *Trans. Faraday Soc.*, 1923, **19**, 38.

molecular volume. A comparison of P for different substances becomes, therefore, a comparison of molecular volumes at temperatures at which the liquids have the same surface tension. Sugden calls the quantity denoted by P the *parachor* (from $\pi\alpha\rho\acute{\alpha}$ = by the side of, and $\chi\omicron\rho\acute{o}s$ = space) to signify comparative volume.

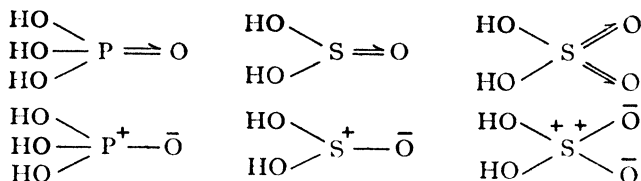
In his first paper Sugden calculated the values of the parachor for 167 compounds for which data on surface tension and density were known. He found that the quantity P is partly additive and partly constitutive, so that it can be calculated by adding together two sets of constants, one of which represents the contribution of the atoms present in the molecule of the compound, whilst the other represents the contribution of abnormal types of linkages. He gives the following table for atomic and structural parachors:

C = 4.8	Triple Bond = 46.6
H = 17.1	Double Bond = 23.2
O = 20.0	O ₂ in esters = 60.0
N = 12.5	
F = 25.7	
Cl = 54.3	
Br = 68.0	
I = 91.0	

In subsequent papers Sugden and his collaborators* have extended their valuable work, and have been able to give experimental evidence in favour of certain structural formulæ in cases where previously only speculation had existed. A brief summary of the results obtained will now be given.

Two kinds of double bond exist which contribute 23.2 and — 1.6 respectively to the value of the parachor. The former kind exists in molecules of substances like ethylene, propylene, acetone, and diethyl ketone, and is considered to be a non-polar double bond due to the sharing between the two atoms concerned of two pairs of electrons: the latter kind exists in molecules of substances like phosphorus oxychloride, triethyl phosphate, sulphuryl chloride, diethyl sulphite, and diethyl sulphate, where the two atoms concerned cannot share two pairs of electrons without one of them obtaining a shell of electrons exceeding eight in number; this type of bond is, therefore, considered to be the semi-polar double bond suggested by Lowry. The formulæ for phosphoric, sulphurous, and sulphuric acids, according to the two methods suggested by Lowry for formulating this type of linkage, are therefore

* Sugden, Reed, and Wilkins, *J. Chem. Soc.*, 1925, 1525; Sugden and Whittaker, *ibid.*, 1925, 1868; Sugden and Wilkins, *ibid.*, 1925, 2517; 1927, 139; Sugden, *ibid.*, 1927, 1173.



The first of these methods, in which a barb indicates the direction in which an electron has been transferred, is considered by Sugden to be preferable because the second method is apt to be confused with other formulæ in current use in which + and - signs are attached to atoms without the precise significance of an electrovalency. We shall consider later (p. 207) a third method of formulation, suggested by Main Smith, which appears to be better than either of these.

It is of interest to note that strong experimental evidence in confirmation of Sugden's (and Lowry's) view that sulphinates and sulfoxides do not contain non-polar double bonds has been obtained by the discovery of a new type of stereoisomerism that occurs with ethyl *p*-toluene sulphinate* and mixed sulfoxides.† These compounds have only three groups attached to the central sulphur atom,

and if they were of the type $\text{O}=\text{S} \begin{array}{l} \diagup \text{OR}_1 \\ \diagdown \text{R}_2 \end{array}$ and $\text{O}=\text{S} \begin{array}{l} \diagup \text{R}_1 \\ \diagdown \text{R}_2 \end{array}$ respectively,

where the oxygen and the sulphur atoms are united by non-polar double bonds, the compounds would be symmetrical and show no optical activity. The circumstance that these compounds can be obtained in optically active forms indicates that their formulæ are

$\bar{\text{O}}-\text{S}^+ \begin{array}{l} \diagup \text{OR}_1 \\ \diagdown \text{R}_2 \end{array}$ and $\bar{\text{O}}-\text{S}^+ \begin{array}{l} \diagup \text{R}_1 \\ \diagdown \text{R}_2 \end{array}$ respectively, the molecules having a

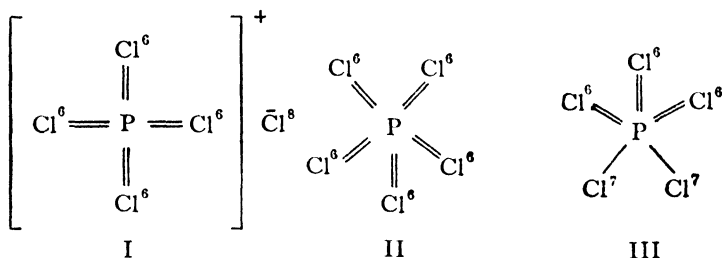
tetrahedral configuration with a positively charged sulphur atom at a corner of the tetrahedron.

Sugden shows further that the parachor of osmium tetroxide indicates that the molecule of this substance has four semipolar double bonds. This is of interest as providing experimental evidence for the octet theory for an element of high atomic number, for had the four double bonds in this substance proved to be non-polar, each bond would involve four electrons and thus give to osmium a shell of sixteen electrons.

* Phillips, *J. Chem. Soc.*, 1925, 2552.

† Harrison, Kenyon, and Phillips, *ibid.*, 1926, 2079.

An examination of the parachors of phosphorus pentachloride and antimony pentachloride gives further evidence that the maximum number of electrons in the outer shell of any atom is eight. Three electronic formulæ which have been suggested for phosphorus pentachloride are shown in the following figure. Each line represents one



shared electron (i.e. half a normal valency bond), and superscript figures indicate the number of unshared electrons in the outer shell of the atom—a convenient symbolism suggested by Main Smith.

Formula I, due to Langmuir, indicates a polar substance and is therefore in conflict with the known properties of phosphorus pentachloride. Formula II has been given by Lewis, who considers that substances of this type do not conform to his "rule of eight". It has been already pointed out (p. 164) that Lewis regards his "rule of two" as being more generally followed than his "rule of eight". Hence, in order to preserve the idea that the single bond is invariably due to a shared pair of electrons, he sacrifices the octet rule, and represents the phosphorus atom with a shell of ten electrons in this compound. Prideaux,* however, maintains the rule of eight by discarding the duplet rule for two of the chlorine atoms which he supposes are each bound by sharing one electron with the phosphorus atom, as shown in Formula III. This type of linkage, involving the sharing of only one electron between two atoms, is called by Sugden a *singlet*; its existence has been surmised by many others.†

The values of the parachor obtained by Sugden for the triple bond and the non-polar double bond have been already mentioned as 46.6 and 23.2 respectively. The parachor of the chemical single bond or duplet linkage is neglected when the atomic constants are

* Prideaux, *Chem. and Industry*, 1923, **42**, 672.

† Stark, *vide p.* 155; Sir J. J. Thomson, *Phil. Mag.*, 1921, **41**, 521; Sir J. Walker, *vide p.* 198; Robinson and Kermack, *vide p.* 190; Main Smith, *Chem. and Ind.*, 1923, 1075; 1924, 323; 1925, 944.

computed, in order to provide an arbitrary zero from which the other linkages are measured. Hence it appears that each pair of electrons above two contributes 23.2 units to the value of the parachor. It is reasonable to suppose that each electron which is shared between two atoms contributes 11.6, so that the contribution of a singlet linkage is -11.6 , being 11.6 less than that of the duplet which forms the arbitrary zero above. Further, it has already been seen that the effect of a semipolar double bond, which consists of a duplet plus an electrovalency, is -1.6 , so that the effect of a semipolar single bond, due to the half electrovalency, would be -0.8 . The total effect of the semipolar single bond should therefore be $-11.6 - 0.8 = -12.4$. The values for the various linkages are shown in the following table:

Linkage.	No of Electrons.	Parachor.
Triple bond	6	46.6
Non-polar double bond ..	4	23.2
Single bond (duplet) ..	2	0
Semipolar double bond ..	2	-1.6
Singlet	1	-11.6
Semipolar single bond ..	1	-12.4

Experimentally Sugden finds that the effect on the parachor of phosphorus pentachloride due to the abnormal linkages is -26.7 , which is fairly close to the predicted effect, viz. -24.8 , of the two semipolar single bonds shown in Formula III. It is widely different from the expected effect of Formula I, viz. -1.6 , and from that of Formula II, viz. $+7.7$.* We have therefore strong evidence that Formula III represents the linkages in phosphorus pentachloride, and that singlet linkages exist.

A similar formula for antimony pentachloride is found, the contribution of the abnormal linkages being -25.7 , i.e. within the experimental error of the predicted value -24.8 . Even in the valency shell of antimony, assumed by some to be large, it appears that the number of electrons does not exceed eight.

We may conclude, therefore, that the duplet rule is not so general as Lewis supposed when he first formulated it, but that two atoms may share odd numbers of electrons. Such bonds may or may not

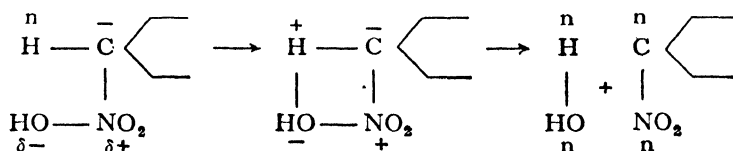
* The effect on the parachor when two extra electrons are shared between six atoms is assumed to be one-third of that found when two extra electrons are shared between two atoms in the non-polar double bond, i.e. $\frac{23.2}{3}$ or 7.7.

develop polarity in the molecule; it is reasonable to suppose that when alternate formulæ are possible, the one showing least polarity is the more probable.

Ingold and Ingold* have adopted the formula of phosphorus pentachloride which has been suggested by Prideaux, and use the conception of the semipolar single bond to explain the mechanism of chlorination by not only this compound but by iodine trichloride and aryl iodide dichlorides as well. They suggest that the symbol for the semipolar single bond should be $\rightarrow$, in which the barb would appear to indicate the transference of half an electronic charge. This arises when a neutral atom shares an electron contributed by another atom, as in the singlet linkages of phosphorus pentachloride. When, however, this symbol is combined with a bond it indicates the transference of a whole electron, as in the case suggested by Lowry and recommended by Sugden of the semipolar double bond, $\Rightarrow$.

This is an example of the difficulty of providing a consistent and convenient nomenclature elastic enough to accommodate itself to the needs of the subject of valency which is developing so rapidly. One has only to be reminded of the fact that the dot is used for one electron and also as an abbreviated bond implying two electrons,† and that the line is also used with these meanings (p. 88), to be aware of further difficulties in the standardization of symbols.

Again, it must be remembered that some chemists desire to indicate a polarity in a molecule less extreme than that caused by the transference of an electron from one part of the molecule to another; nevertheless these chemists have used $+$ and $-$ signs to indicate this intramolecular polarity. Ingold and Ingold‡ have used the terms *incipient* polarization and *incipiently* ionized molecule to describe such cases, and have used the symbols $\delta+$ and $\delta-$ to signify small fractions of a unit charge. These authors reserve the signs $+$ and $-$ to connote unit charges, whilst n indicates neutrality. Thus the mechanism of *op*-substitution by positive groups is illustrated as follows:

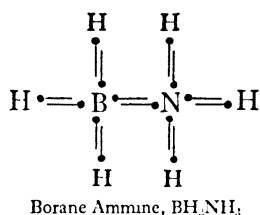
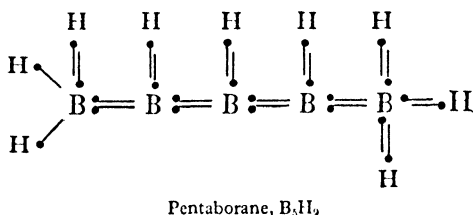
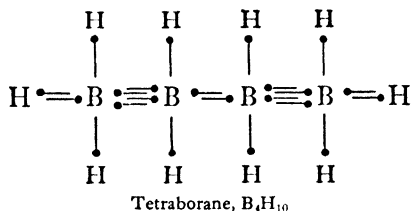
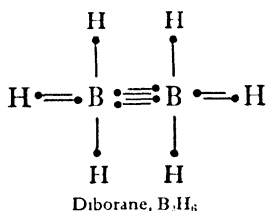


* Ingold and Ingold, *J. Chem. Soc.*, 1926, 1315.

† Not to mention its use as indicating an ion, e.g. Na^+ .

‡ *Loc. cit.*

Further examples of a bond consisting of one shared electron are furnished by the hydroborons.* In working out the constitution of these compounds, Main Smith has been guided by the general principle that a hydrogen atom is bound by two electrons only when it is replaceable by a halogen atom; he infers that when the hydrogen atom is not so replaceable it is bound by a singlet bond. He gives formulæ for boron compounds which introduce a new symbol $\text{---}\cdot$, as, for example,



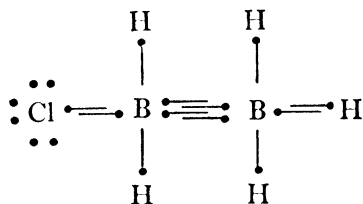
Each line represents a shared electron, and is terminated by a dot at the end nearest to the atom to which the electron belonged. This symbol makes it easy to analyze the compound so as to determine any intramolecular ionization that may have occurred. For example, each hydrogen atom in combination with a boron atom by means of a singlet bond is readily seen to be charged positively with half an electronic charge since the electron proper to it in its neutral free state is now shared with a boron atom. Further, by this method of formulation, the maximum possible valency of the atom is the total number of dots around it; the valency actually in operation is the number of dots that terminate dashes; whilst the contravalency actually in operation is the number of dashes that are not dotted at the end nearest to that atom.

This method of formulation is very attractive, and, if generally adopted, would go far to remove the present ambiguities which exist in the symbols that represent valency bonds.† It has the merit

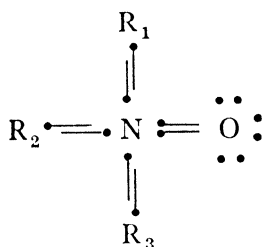
* J. D. Main Smith, *Chem. News*, 1927, 135, 81.

† Cranston, *Chemistry and Industry*, 1928, 208.

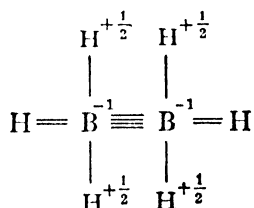
of introducing an entirely new symbol, which indicates in a simple and obvious manner both the singlet type of bond and the atom to which the electron involved originally belonged, so that any intramolecular polarization which may result can be readily calculated. Further, the symbol can readily be repeated two, three, or four times to represent the duplet, triplet, and non-polar double bond respectively. If it is considered desirable to indicate unshared electrons these may be shown as dots. Thus Main Smith gives to chlorodiborane, B_2H_5Cl , the formula



The semipolar double bond can be represented without ambiguity, as, for example, in the following formula for an amine oxide.



It is of interest to note that the constitution of diborane given by Main Smith above was put forward by Sugden independently. The formula,



however, that Sugden gives is not so neat, as it requires superscript numbers to indicate the polarization of the molecule.

Some of the advantages of the use of the symbol $\text{---}\bullet$ may be summarized as follows:

1. It enables all the types of electronic bonds so far recognized by chemists to be graphically represented in a consistent way. (The symbol is flexible enough even to show "incipient polarization" if required. Thus a slightly ionized molecule of HCl may be shown with the electron proper to the hydrogen atom a short distance along the line, e.g. $\text{H} \text{---}\bullet \text{Cl}$.)

2. It shows that the ordinary chemical bond or duplet linkage is a dual entity.

3. It shows that the semipolar double bond is a dual entity.

4. It shows that the duplet linkage differs from the semipolar double bond, because the former is a reciprocal affair between the atoms, whilst the latter is not.

5. It can represent the sharing between two atoms of an electron which has been furnished by neither.

6. It shows readily the residual charge on each atom in a molecule, providing it is assumed that when electrons are shared the sharing is equal. This charge is the difference between the number of electrons in the valency shell of the neutral atom before combination and the sum of the unshared electrons plus half the shared electrons after combination, all of which information is obtainable from the formula. The symbol does not necessarily prejudge the question of the distribution of the electrical charge, because the above assumption need not be made.

It has been pointed out by Main Smith that:

7. It shows the maximum possible valency as the total number of dots round the atom.

8. It shows the valency actually in operation as the number of dots at the near ends of dashes.

9. It shows the contra-valencies actually in operation as the number of lines that are not dotted at the atom end.

CHAPTER VIII

Symbols in Physical Chemistry

The growth of physical chemistry during the last half-century or more has required the introduction of new symbols, or a new use of old ones. An attempt will therefore be made to gather together here the symbols employed in physical chemistry, except those which are of purely mathematical or physical significance.

Symbols and Notation of Thermochemistry.—The unit of heat is a calorie, but there are calories of three different magnitudes. The mean gramme-calorie, which is 1/100th part of the heat necessary to raise 1 gm. of water from 1° to 100° C., and practically equal to the heat necessary to raise 1 gm. of water from 14·5° to 15·5° C., is written cal., or simply C.; the kilogram-calorie, a thousand times this value, receives the symbol Cal.; whilst the heat necessary to raise 1 gm. of water from 1° to 100° C. is expressed as K. Thus, for practical purposes

$$\text{Cal.} = 10\text{K} = 1000 \text{ cal.}$$

The small calorie, cal., is the unit most frequently in use.

The notation of thermochemistry is due chiefly to Julius Thomsen.*

Instead of the calorie, which is an arbitrary unit, depending on a property of water, Ostwald prefers to use the erg, which is the absolute unit of energy. Since, however, the erg itself is too small for actual use, he has introduced a unit called the kilojoule, $\text{Kj} = 10^{10}$ ergs. Then $1 \text{ cal.} = 0\cdot00413 \text{ Kj}$, or $1 \text{ Kj} = 239\cdot1 \text{ cal.}$

Thomsen distinguishes thermochemical formulæ by writing the indices above instead of below the ordinary symbols, the formulæ themselves indicating gramme-molecules. Thus the formula H^1_2O signifies 18 gm. of water concerned in a thermochemical change. When a reaction occurs in solution, the amount of water present

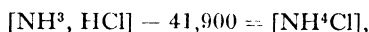
* *Thermochemische Untersuchungen*, Leipzig, 1882-6.

being sufficient to prevent thermal change when more is added, the symbol Aq is used. Thus CuSO_4Aq signifies an aqueous solution of copper sulphate, and CuSO_4Aq , a gramme-molecular weight of such a solution in relation to thermochemical change. Reacting quantities are generally, but not inevitably, enclosed in square brackets, and the components of a reaction separated by a comma. Thus:



signifies that when 17 gm. of ammonia combine with 36.5 gm. of hydrogen chloride, both at a specified temperature, to produce 53.5 gm. of NH_4Cl at the same temperature, 41,900 cal. are evolved.

The equation may, however, be transposed thus:

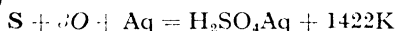


the significance of this statement being that the system $[\text{NH}_3, \text{HCl}]$ contains energy in excess of that contained in the system $[\text{NH}_4\text{Cl}]$ amounting to 41,900 cal. Nothing is stated or known concerning the total energy in either system.

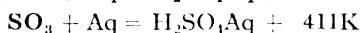
Occasionally the solid, liquid, and gaseous states are represented by the use of formulæ of different types. Thus ordinary type may stand for the liquid state, thick type for the solid state, and italics for the gaseous state.

So $\text{H}_2\text{O} - \text{H}_2\text{O} = 1440 \text{ cal.}$, and $\text{H}_2\text{O} - \text{H}_2\text{O} = 9670 \text{ cal.}$, represent respectively the latent heats of fusion of ice, and vaporization of water, or, more simply, the latent heats of water and steam.

Similarly,

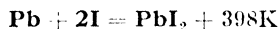


and

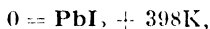


and subtracting $\text{S} + 2\text{O} - \text{SO}_3 \div 1011\text{K} (= 101,100 \text{ c.l.})$.

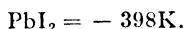
The heat of formation of a compound, e.g. lead iodide, is represented thus:



If we write



such an equation signifies that starting from the system $(\text{Pb} + 2\text{I})$ as representing zero level of energy, i.e. ignoring the unknown quantity of energy contained in this system, 398K are evolved when the system (PbI_2) is produced, so that this system contains an amount of energy less than the system $(\text{Pb} + 2\text{I})$ equal to 398K. This fact is otherwise expressed thus:



Symbols employed in Chemical Dynamics.—Probably the fundamental conception of modern physical chemistry is that of dynamical equilibrium, that is of an equilibrium reached when reactions tending in two opposite directions become balanced. If this is so, then the first symbol to be considered is that of the reversibility of a reaction. Such a symbol or sign was introduced by van't Hoff.*

Consider a reaction such as:



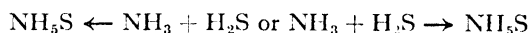
The sign $=$ does not say what is happening; it merely indicates that ammonium hydrogen sulphide can be converted quantitatively without loss into a mixture of ammonia and hydrogen sulphide, one molecular proportion of each compound being concerned in the reaction. Van't Hoff, however, replaces the sign $=$ by the sign $\rightleftharpoons$ which “represents pictorially what is conceived to be the mechanism” of a reversible reaction in which ammonium hydrogen sulphide is dissociated into ammonia and hydrogen sulphide at the same rate that these gases combine to reproduce the original substance. The sign is therefore pragmatic; it represents something doing, a chemical equilibrium which is dynamic, because it results from the simultaneous occurrence of equal and opposite reactions.

This sign can be divided into two parts, viz.: $\rightarrow$ and $\leftarrow$.

Thus



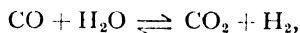
represents dissociation, and



association.

In modern use the inner barb of each arrow is generally removed, so that the sign becomes $\rightleftharpoons$. This alteration was suggested by H. Marshall † to make the sign more compact. Marshall also proposed the symbol $\Rightarrow$ for an irreversible change, $\rightleftharpoons$ for a reaction but slightly reversible, and $\rightleftharpoons$ for a reaction reversible at a definite transition temperature, such as an allotropic change.

J. W. Mellor ‡ points out that the sign of reversibility is a brief way of expressing what could otherwise only be expressed cum-brously. Thus consider the reaction:

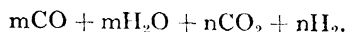


* *Vide Lectures on Theoretical and Physical Chemistry*, Part I.

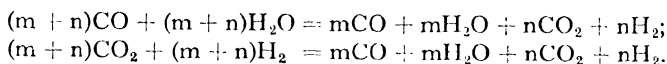
† *Zeit. phys. Chem.*, 1902, **41**, 103.

‡ *Chemical Statics and Dynamics*, 1904, p. 80.

occurring at a suitably high temperature. When equilibrium is attained all four molecular species will be present, CO and H₂O in one molecular proportion and CO₂ and H₂ in another. Let the molecules present when the condition of equilibrium is attained be as follows:



This condition will be reached from either side by one or other of the reactions:

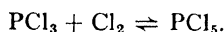


These are the cumbrous expressions which are avoided by the use of the sign $\rightleftharpoons$ in the above brief equation.

Closely connected with the subject of reversible reactions is the law of mass action which states that the extent to which a substance reacts depends upon its "affinity" and "active mass". Active mass is another name for molecular concentration within the sphere of chemical action, i.e. the number of molecules per unit volume.

The symbol C is used for concentration, so that C_m is the concentration of molecules of the *m* kind.

Consider the thermal dissociation of phosphorus pentachloride, and suppose that equilibrium has been reached at a fixed temperature, this state being represented by the equation:



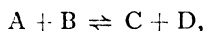
Let the concentrations of the three kinds of molecules be C_{PCl₅}, C_{PCl₃}, C_{Cl₂}; then the rate at which PCl₃ and Cl₂ combine depends upon C_{PCl₃} and C_{Cl₂}, i.e. upon their product, and is therefore equal to this product multiplied by a constant, say *k*₁, i.e. to *k*₁ × C_{PCl₃} × C_{Cl₂}. Similarly the rate at which PCl₅ dissociates is equal to *k*₂ × C_{PCl₅}. When there is equilibrium these two quantities are equal, i.e.

$$k_1 \times C_{\text{PCl}_3} \times C_{\text{Cl}_2} = k_2 \times C_{\text{PCl}_5}; \text{ or } \frac{C_{\text{PCl}_3} \times C_{\text{Cl}_2}}{C_{\text{PCl}_5}} = \frac{k_2}{k_1} = K \text{ say.}$$

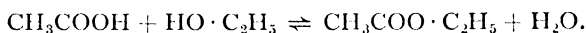
The value of *K* depends in this case upon the temperature at which equilibrium is maintained, as well as upon the intrinsic properties of the reactants; but the whole expression shows what relation must be maintained between the concentrations of the three kinds of molecules for equilibrium to persist, i.e. that with C_{PCl₅} constant C_{PCl₃} must increase in the same ratio as C_{Cl₂} decreases or vice versa, and that if C_{PCl₅} increases it must be in the same ratio as the product C_{PCl₃} × C_{Cl₂} increases or vice versa.

Here is another example illustrating the same principle and a similar use of symbols:

Consider the reaction



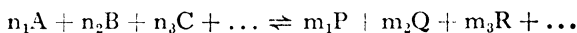
which might be for example:



The general equation is:

$$k_1 C_A C_B = k_2 C_C C_D, \text{ or } \frac{C_A C_B}{C_C C_D} = \frac{k_2}{k_1} = K.$$

When, instead of one, n molecules of any substance participate in a reaction the value of the constant varies as the n th power of the concentration of the molecular species concerned. Thus consider the general reaction:



the value of the constant at a certain temperature is:

$$\frac{C_A^{n_1} \times C_B^{n_2} \times C_C^{n_3} \times \dots}{C_P^{m_1} \times C_Q^{m_2} \times C_R^{m_3} \times \dots} = K.$$

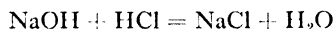
In the case of gases, since pressure is proportional to concentration, the symbol P may replace C . An alternative way of representing molecular concentration is to employ square brackets instead of the sign C with a suffix. Thus the equilibrium equation for the dissociation of PCl_5 becomes:

$$\frac{[\text{PCl}_3] \times [\text{Cl}_2]}{[\text{PCl}_5]} = K,$$

and similarly, the above general equation becomes:

$$\frac{[A]^{n_1} \times [B]^{n_2} \times [C]^{n_3} \times \dots}{[P]^{m_1} \times [Q]^{m_2} \times [R]^{m_3} \times \dots} = K.$$

The Electrolytic Dissociation Theory.—The essential change in the conception of a chemical reaction involved in the electrolytic dissociation theory of Arrhenius was that reactions between electrolytes in aqueous solution were reactions not between molecules, but between ions. Thus the reaction of neutralization represented by the equation:



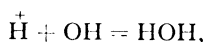
was understood to be a reaction between ions, of which there were

four kinds; viz. those of sodium, hydroxide, hydrogen, and chloride. Moreover these ions were electrolytically charged, either positively or negatively, the algebraic sum of the charges associated with each substance being zero.

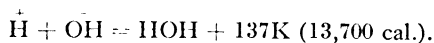
Consequently these charges were first represented by $+$ or $-$ signs set above the symbols of atoms or radicals so that these became the symbols of ions. Thus the above equation of neutralization became:



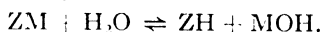
Then it was apparent that $\overset{+}{\text{Na}}$ and $\overset{-}{\text{Cl}}$ were common to both sides of the equation so that the actual reaction was:



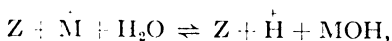
a conclusion which was supported by the fact that the heat of neutralization of all strong bases and acids was constant; thus:



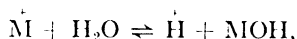
A further example of such symbolism is given by van't Hoff's expression for salt hydrolysis*:



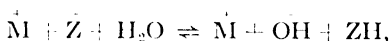
The hydrolysis of a salt of a weak base and a strong acid is represented thus:



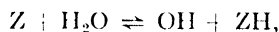
or



the solution becoming acid owing to free hydron; whilst the hydrolysis of the salt of a strong base and a weak acid is represented in this way:



or

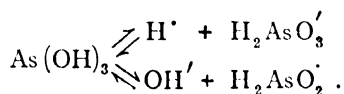


the solution becoming alkaline owing to hydroxide ion.

The method of representing ions by $+$ and $-$ signs, placed vertically above the symbols, has now fallen into disuse. In modern use the signs are smaller, and are placed at the sides of the symbols, thus: Na^+ , Cl^- , or else are replaced by a dot and dash respectively,

* *Lectures*, I, 128.

thus: Na', Cl'. Consequently, as an example, the ionization in two different ways of $\text{As}(\text{OH})_3$ may be represented thus:



With regard to this kind of symbolism it must be remarked that previously the dash was used to indicate the numerical value of valency of whatever kind, as for example in Fe'' , Fe''' , SO_4'' , PO_4''' . Sometimes, however, + and - signs are used to express the valencies of metallic and acidic ions, e.g. Fe^{++} , Fe^{+++} , $\text{SO}_4^{=}$, $\text{PO}_4^{=}$.

Since ions in their behaviour sometimes accord with the law of mass action, their symbols are enclosed in square brackets when equilibrium dependent on concentration is to be represented. Thus if in the above example pertaining to a solution of arsenious hydroxide K_a is the acidic, and K_b the basic dissociation constant, the values of these constants are thus expressed:

$$K_a = \frac{[\text{H}'] [\text{H}_2\text{AsO}_3']}{[\text{As}(\text{OH})_3]}; \quad K_b = \frac{[\text{OH}'] [\text{H}_2\text{AsO}_2']}{[\text{As}(\text{OH})_3]}.$$

Hydrogen-ion or "hydrion" concentration—The measurement of "hydrion" concentration has now assumed great importance in physical and bio-chemistry, so that attention must be paid to the symbol used to express it. The symbol of hydrion is $[\text{H}']$ or $[\text{H}^+]$, the latter being the form in current use in America.

Hydrion concentration is an expression of acidity; but neutrality does not correspond with a zero value because water, which is the standard neutral substance, is ionized to the extent that $[\text{H}'] = [\text{OH}'] = 10^{-7}$. Thus for water $\log[\text{H}'] = -7$ or $-\log[\text{H}'] = 7$.

For $-\log[\text{H}']$ S. P. L. Sørensen* introduced the symbol p_{H}^+ ; this was modified to P_{h} , but now takes the form pH, so that the "pH value of a solution" has become a common phrase in physico-chemical and bio-chemical literature. The pH value for absolute neutrality is 7.07; moreover this value decreases as a solution becomes acid, and increases as it becomes alkaline, because the number is really a negative index of hydrion concentration.

* *Biochem. Zeit.*, 1909, 21, 131.

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