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Electrons, Atoms and Molecules.¹

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ANY one who is familiar with the state of chemistry before and after the War must recognise that, whilst chemical practice and chemical beliefs have undergone very little alteration, the foundation underlying these beliefs has been altered profoundly by recent physical discoveries. In particular, although chemists still believe in Dalton's atoms and in the molecules of Avogadro, they have been compelled to accept an entirely different picture of the structure of the atom, and to adopt a new and revolutionary conception of the nature of the forces which bind the atoms together into molecules. Whilst, therefore, chemical research still proceeds along familiar paths, and is expressed by means of familiar terms and symbols, physical research has given us a new outlook; and, since what a man does is ultimately determined by what he believes, it is certain that chemical practice as well as chemical theory must be influenced profoundly by the new ideas that have been given to us by our physical colleagues. The object of this discourse is to indicate some of the aspects of pre-War chemistry which have been transformed by the impact of post-War physics.

MOLECULAR DIMENSIONS.

The principal contribution of the physicist to our knowledge of molecules has been a numerical one. He has taught us how to count, to weigh, and to measure individual molecules, and, in the person of Sir William Bragg, he has provided us with a convenient system of units in which to express these quantities. This system is based upon Ångström's unit of length, 10^{-8} cm., which has long been used in order to express the wave-lengths of light of different colours. Bragg has, therefore, proposed² to measure areas and volumes in 10^{-16} sq. cm. and 10^{-24} c.c.; and although it is scarcely possible to picture the process of filling with water a vessel with a capacity of only 10^{-24} c.c., it is, nevertheless, an obvious step to make the unit of mass correspond with the unit of volume, as 10^{-24} gram.

Having got a suitable system of units, we can use them in order to express atomic and molecular dimen-

sions. The fundamental constant in this investigation is the *Avogadro number*, which tells us the actual number of atoms in the gram-atom of any element, or of molecules in the gram-molecule of any element or compound. Unlike Loschmidt's number (which tells us how many molecules there are in 1 c.c. of a gas at normal temperature and pressure), this is a universal constant, since it is not influenced by deviations from the ideal gas laws. During the past twenty years, more than a score of attempts have been made to determine the numerical value of this constant, by the most diverse methods; but I need only quote the number finally deduced by Millikan in 1917 from a study of the movement of a rain of electrified oil-drops. This curiously indirect method has given surprisingly accurate results; indeed, it is said that the number of molecules in a gram-molecule of a pure substance is known with about the same degree of accuracy as the total population recorded in the census of a big city such as Chicago. In conformity with our scheme, Millikan's value of the Avogadro constant can be expressed most conveniently in powers of eight as $N = 0.6062 \times 10^{24}$.

By taking the reciprocal of this number we can deduce at once that *the weight of an individual atom or molecule in Angström units is 1.65 times its atomic or molecular weight*. For example, the mass of an atom of hydrogen is $1.65 \times 1.0075 = 1.66$ Å.U.; and the mass of a molecule of oxygen is $1.65 \times 32 = 52.8$ Å.U. From these data it would be easy to calculate the linear dimensions of the molecule if we could assume that it was spherical or cubical; but, although the early experiments of Devaux supported this view, more exact measurements have proved that the dimensions of the molecule are not equal in different directions. The molecule has, in fact, a definite shape, now open to experimental investigation, which must be taken into account in calculating its dimensions. Let me indicate three physical methods used for this purpose.

(a) *Viscosity of Gases*.—According to the kinetic theory of gases, the viscosity of a gas is a measure of the sectional area of the molecules. This was one of the earliest methods used to calculate molecular dimensions, and (unlike the two following methods)

¹ Compiled from lectures delivered at the Birkbeck College, London, on Jan. 25, and at Bristol on Feb. 12, 1926.

² *Proc. Phys. Soc.*, 1921, 34, p. 35.

it is independent of a knowledge of the Avogadro constant. It has been developed in recent years by Prof. Rankine, who has deduced for the *collision-areas* of various gases values such as the following :

TABLE I.—COLLISION-AREAS OF GASES IN ÅNGSTRÖM UNITS.³

CH ₄ = 7.72	NH ₃ = 6.40	OH ₂ = ?	HF = ?	Ne = 4.17
SiH ₄ = ?	PH ₃ = 9.11	SH ₂ = 7.73	HCl = 6.76	A = 6.48
	AsH ₃ = 9.85	SeH ₂ = ?	HBr = 7.63	Kr = 7.57
	SbH ₃ = ?	TeH ₂ = ?	HI = 9.26	X = 9.15

These numbers, however, do not lead directly to a knowledge of the linear dimensions of the molecules, since they merely give the average area of the molecule as viewed from every possible aspect.

(b) *Monomolecular Films*.—Much more detailed information is given by a study of thin films of oil on the surface of water. So long ago as 1899,⁴ Lord Rayleigh explained the fact that a definite concentration of oil was required in order to diminish the surface tension of water by supposing that it was necessary to cover the water with a film of oil one molecule thick, before any effect could be produced. Since the quantity required corresponded with a film of a thickness of about 10 Å.U., he concluded that this was the approximate diameter of the molecules.

When the Avogadro number was known it was possible to compare the *thickness* of the monomolecular film with the *area* occupied by the individual molecules, and thus to get some idea of their shape. Devaux, who first made this comparison in 1904,⁵ was unfortunate in that the triolein with which he worked gave a monomolecular film with a thickness of 11 Å.U., as compared with a calculated molecular diameter of 11.3 Å.U. He therefore concluded that the molecules were roughly spherical in shape, as Rayleigh had postulated; and it was left to Langmuir in 1917⁶ to discover that the dimensions of the molecule are in fact widely different in different directions. Thus in Table II. the molecular

TABLE II.—CROSS-SECTIONS AND LENGTHS OF MOLECULES.

Substance.	Formula.	Area per Molecule.	Width.	Length.	Length per Carbon Atom.
Palmitic acid	C ₁₅ H ₃₁ COOH	21 Å.U.	4.6 Å.U.	24.0 Å.U.	1.5 Å.U.
Stearic acid	C ₁₇ H ₃₅ COOH	22	4.7	25.0	1.39
Cerotic acid	C ₂₅ H ₅₁ COOH	25	5.0	31.0	1.20
Tristearin	(C ₁₈ H ₃₅ O ₂) ₃ C ₃ H ₅	66	8.1	25.0	1.32
Myricyl alcohol	C ₃₀ H ₆₁ OH	27	5.2	41.0	1.37

area was deduced directly by dividing the total area of the film in Å.U. by the number of molecules which it contained; the width is merely the square-root of this area; but the length was calculated on the assumption that the density of the film is equal to that

of the oil in bulk, and that the length of the molecule is equal to the thickness of the film.

To Langmuir, then, belongs the credit of discovering that, whilst the sectional area of the molecule of a saturated fatty acid or alcohol is approximately constant, corresponding with a square with a side of about 5 Å.U.,⁷ the length of the chain may extend to more than 40 Å.U. As a result of these observations, Langmuir was also able to assert that the individual molecules in the film were oriented, with the acid radical immersed in the water and the hydrocarbon chain projecting outwards towards the air. The spreading of the oil into a monomolecular film could therefore be attributed to the striving of the 'hydrophilous' or thirsty 'heads' of the molecules to secure access to the water, and of the 'hydrophobic' or oily tails to escape drowning.

Most of the applications of Langmuir's conception are physical in character, as in the case of the lowering of the surface tension of water by a film of oil. Harker, however, has recently put forward a case⁸ in which the chemical properties of a compound appear to be determined by the orientation of the molecules in the surface of the liquid. Thus, he found that benzyl chloride could not be hydrolysed by dry steam, but was rapidly hydrolysed whenever there was an opportunity for liquid water to condense. This result can be explained most easily by supposing that the steam could not secure access to the active 'heads' of the molecules, since these would normally be directed towards the interior of the liquid, but that liquid water can reverse this orientation, and thus bring the chlorine into a position in which it can be attacked.

(c) *X-ray Analysis*.—The third method depends on investigating the distance between the mass-centres of atoms or molecules by means of X-rays. This is a reciprocal process, since our knowledge of the wavelengths of X-rays does not yet rest on direct measurements of length, but has been deduced indirectly from the distance between the atoms of sodium and chlorine in a crystal of rock-salt, as calculated with the help of Avogadro's constant. Thus, since one gram-molecule of salt occupies 27 c.c., it is clear that the total number of atoms of sodium and chlorine in 1 c.c. of salt is $2/27 \times 0.6062 \times 10^{24} = 0.0452 \times 10^{24}$; but, before we can calculate the distance between the centres of these atoms, we must know how they are arranged in the crystal. A preliminary survey by means of X-rays shows that the atoms of sodium and chlorine occupy alternate points in a simple cubic lattice; we can, therefore, allot to each atom a cubic cell with a volume

³ *Trans. Faraday Soc.*, 1922, **17**, 720.

⁴ *Phil. Mag.*, 1899, **48**, 331.

⁵ *Proc. Soc. Phys. Bordeaux*, April 1904; compare Smithsonian Inst. Report, 1913, 261.

⁶ *J. Amer. Chem. Soc.*, 1917, **39**, 1848.

⁷ The more exact measurements of Adam (*Proc. R.S.*, 1922, **A**, **101**, 452, 516 *et seq.*) have shown that the sectional area of the hydrocarbon chain is 21.0 Å.U., but that the 'head' of the molecule occupies an area of 21.7 Å.U. in the alcohols, and of 25.1 Å.U. in the fatty acids.

⁸ *J.C.S.*, 1924, **125**, 500.

of 22.1×10^{-24} c.c. (the reciprocal of the preceding number); and by taking the cube root of this number we can deduce the distance between the atoms as 2.81 Å.U. After having determined this fundamental distance, we can use a crystal of rock-salt⁹ as a diffraction grating in order to determine the wave-lengths of the X-rays emitted by the elements, and we can then use these wave-lengths in order to determine the distance between the atoms or molecules in other crystals. In this way it has been shown, for example, that the distance between the carbon-atoms in a diamond is 1.52 Å.U., and that the same 'atomic diameter' appears incessantly in other carbon-compounds. This diameter, indeed, is one of the most constant of the numerical properties of the element, and is the obvious basis for a modern space-chemistry of carbon compounds.

STEREOCHEMISTRY.

In addition to providing information as to the distance between atoms and molecules, X-ray analysis has made important contributions to our knowledge of molecular configuration or 'chemistry in space.' The first of the new chemical space-models was developed in 1874 by le Bel and Van 't Hoff, in order to account for the limited number of isomers which can be prepared of carbon compounds of various types. Thus since isomerism in derivatives of methane first appears in compounds of the type CHXYZ, these authors were led independently to postulate a *tetrahedral* configuration of the four univalent radicals around a central atom of carbon, in place of the *square* configuration of the common two-dimensional formulæ. The two opposite ways in which the four different radicals in these 'asymmetric' compounds can be arranged in space about the central atom of carbon could then be represented by alternative symbols, corresponding with the two known isomers, as follows:

The new three-dimensional formulæ were confirmed by the experiments which led to the enunciation of von Baeyer's *Strain theory*, since it was found that a 5-atom ring with angles of 108° is more easily formed than a 4-atom ring with angles of 90° , as would be expected if the normal angle between the bonds is the characteristic tetrahedral angle, $109\frac{1}{2}^\circ$, of the solid model, instead of the right-angle of the planar formulæ.

Our exact knowledge of the wave-length of X-rays was formerly limited in the upward direction to about 15 Å.U., because no suitable crystals of larger molecular dimensions were available to provide a grating for their investigation. Thoriaus and Siegbahn (*Ark. f. Mat. Astron. och Fysik*, Stockholm, 1925, 19, 12), however, have recently measured wave-lengths up to 21 Å.U. by using as a grating a crystal of palmitic acid for which $2d = 71.19$ Å.U.

This chemical evidence has now been confirmed by direct physical measurements. In particular, X-ray analysis has proved that the diamond is built from tetrahedrally-oriented atoms, and in such a simple manner that a child of five, if provided with a supply of rods and balls with properly adjusted sockets, could not build the model differently. A similar tetrahedral configuration of four beryllium atoms around a central atom of oxygen, and conversely of four oxygen atoms around a central atom of beryllium, has been found in basic beryllium acetate,¹⁰ $\text{OBe}_4(\text{O}_2\text{CMe})_6$; and the X-ray analysis of ice¹¹ shows four hydrogen atoms arranged in the same tetrahedral pattern about each atom of oxygen. A tetrahedral arrangement of four oxygen atoms around a central atom of sulphur has also been found in barium sulphate.¹²

Moreover, in addition to confirming and extending the scope of Van 't Hoff's tetrahedral configuration, X-ray analysis has also indicated the existence of other configurations. Thus in ice, every atom of hydrogen is placed at the centre of a line joining two oxygen atoms, thus giving rise to a *linear* configuration,

Again, in sodium nitrate, and in calcite and aragonite, we find a *triangular* configuration, of three oxygen atoms about a central coplanar atom of nitrogen or of carbon, the three oxygen atoms being ranged symmetrically about a trigonal axis, as in the schemes

In order to preserve this trigonal symmetry, the ions in the crystal have been formulated¹³ as

instead of $\text{O}=\text{N}=\text{O}$ and $\text{O}=\text{C}=\text{O}$

This planar configuration has been observed also in the acetate groups of basic beryllium acetate, where the two oxygen atoms are arranged symmetrically about a digonal axis, *e.g.*, as in

Moreover, graphite, which was thought at one time

¹⁰ Bragg and Morgan, *Proc. R.S.*, 1923, A, 104, 437.

¹¹ Bragg, *Proc. Phys. Soc.*, 1922, 34, 98.

¹² James and Wood, *Manchester Memoirs*, 1924-5, 69, No. 5.

¹³ *Trans. Faraday Soc.*, 1923, 18, 285. In these symmetrical formulæ the central atom carries only a sextet of electrons: this condition is, therefore, probably unstable except in the crystals, where the anion is surrounded symmetrically by six oppositely charged cations.

to contain the same zigzag network of atoms that can be recognised in successive layers of a diamond, is now reported to contain a *flat* network of hexagons.¹⁴ Since graphite has the structure of an aromatic hydrocarbon, and actually gives rise to mellitic acid $C_6(CO_2H)_6$ on oxidation, it is difficult to resist the conclusion that the characteristic form of the benzene ring may after all be the traditional 2-dimensional hexagon rather than a zigzag hexagon in three dimensions.

CONFIGURATION OF CO-ORDINATION COMPOUNDS.

As in the case of carbon, the X-ray analysis of co-ordination compounds has proved the correctness of a configuration which had been deduced previously by purely chemical methods. Many years ago Werner concluded that the six chlorine atoms of potassium platini-chloride, $K_2[PtCl_6]$, are all grouped round a central atom of platinum, instead of forming two groups, as in the formula, $2KCl, PtCl_4$. By studying the number of isomers that could be prepared of co-ordination compounds of different types, he was able to assign an *octahedral* configuration to the six co-ordinated radicals. Thus the existence of two isomers of the type MX_4Y_2 follows at once from the fact that substituents may occupy adjacent or opposite apices of the octahedron.

Werner's theory was finally established by the discovery, in compounds such as the cobalti-oxalates, $K_3[Co(C_2O_4)_3]$, of a new type of optical activity, which no one else had even suspected to be possible. This optical activity can, however, be explained immediately by means of an octahedral model, as in the following projection,¹⁵ where the thick lines indicate the positions of the three oxalate groups.

X-ray analysis has now revealed, by direct mensuration, an octahedral configuration of the six halogen atoms in $K_2[SnCl_6]$, $(NH_4)_2[SnCl_6]$, $(NH_4)_2[PtCl_6]$, $K_2[PtCl_6]$

and $(NH_4)_2[SiF_6]$, as well as of the six atoms of chlorine which surround each atom of sodium in a crystal of rock salt. Even more important is the proof that the six molecules of ammonia in the ammoniate $NiCl_2 \cdot 6NH_3$, are arranged in an octahedral pattern about the central atom of nickel,¹⁶ since this confirms in the minutest detail the formulation of the compound as an *ammine* of the type $[Ni \cdot 6NH_3]Cl_2$. Modern physics has thus provided a new and very secure foundation for an important item of belief, which has only recently been added to the chemists' creed.

IONISATION.

During a period of forty years, physical chemists have asserted that when an electrolyte is dissolved in water it is partially dissociated into free ions

No adequate basis was provided for this "nonsensical hypothesis" (as Prof. Armstrong described it in a letter to NATURE of November 26, 1896), "which asserts that hydrogen chloride and a few other compounds are so loosely strung together that they fall to pieces when dissolved in water: out of sheer fright it would seem, as no valid motive is suggested for such self-sacrifice." An excuse for this strange conduct was afterwards found in the affinity of the ions for water; but at the time the 'dissociationists' preferred to use the 'blessed word' *allotropy*¹⁷ as a mask to conceal the difficulty of explaining the supposed indifference towards one another of oppositely charged atoms of sodium and chlorine, as contrasted with the violent interaction of metallic sodium with gaseous chlorine and the still more violent interaction that might be expected between the atoms of the two elements. The more concrete suggestion that "the atoms of the dissolving electrolyte evolve heat by combining with their electric charges,"¹⁸ was laughed out of court as being absurdly opposed to sound physical doctrine, since experience had shown that energy was always used up in the electrification of matter, and that the energy required to impart a given charge to a spherical conductor was inversely proportional to its diameter, and must therefore be enormous in the case of single atoms.

Modern physics has turned this problem inside out, since it is the molecules, and not the ions, of a salt of which the existence is now questioned. Thus, according to current views, the metals are so ready to lose electrons and the non-metals to gain them, that the ions of a salt are more stable than the corresponding neutral atoms. It is therefore impossible for these ions to neutralise their opposite electrical charges in

¹⁴ Bernal, *Proc. R.S.*, 1924, A, **106**, 749; Hull, *Phys. Rev.*, 1917, **10**, 661; Debye and Scherrer, *Phys. Zeitschr.*, 1917, **18**, 291.

¹⁵ *Chemistry and Industry*, March 9, 1923, **42**, 224. This projection, which I suggested in 1923 as a substitute for that used by Werner, has the same hexagonal outline as the diagram commonly used to represent the derivatives of benzene. It has the advantage of showing clearly that the metallic atom in the cobalti-oxalates is dissymmetric, but not asymmetric, since the model has one axis of 3-fold symmetry and three axes of 2-fold symmetry.

¹⁶ Wyckoff, *J.A.C.S.*, 1922, **44**, 1239.

¹⁷ Ostwald, "B.A. Report," 1890, 333.

¹⁸ NATURE, Dec. 17, 1896, p. 151.

order to produce a neutral molecule of salt. The utmost that can be done is for two oppositely charged ions to cling together to form a loose doublet, which is always free to interchange ions with another similar doublet. This state of affairs prevails no doubt in the vapour, as well as in concentrated aqueous solutions. Dilution with water then produces a real 'electrolytic dissociation,' $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$, in which ready-formed ions are merely separated from one another, *e.g.* by the intrusion of molecules of the solvent, instead of being created *de novo* from neutral molecules.

This revolutionary doctrine is supported by the X-ray analysis of salt, which reveals the fact that every atom of sodium is surrounded symmetrically by six atoms of chlorine and conversely. Since there is no difference in the distances which separate a given atom of sodium from six neighbouring atoms of chlorine, there is no experimental justification for asserting that any one of these atoms is combined selectively with the central atom of sodium to form a molecule. On the other hand, crystallographers state that the crystal of salt is not holohedral like Bragg's model, but hemihedral, so that there may be some factor in the structure of the crystal which is not revealed by examination with X-rays.

Physical chemists have not been slow in following up the lead thus given, and have been able to prove that many of the properties of dilute salt solutions can be explained by the *electrostriction* between oppositely charged ions, distributed just as in a crystal of rock-salt, but in a more irregular manner and at a greater average distance from one another.

CHEMICAL AFFINITY.

The combination of unlike elements, *e.g.* of metals with non-metals, which is so important in inorganic chemistry, was explained some twenty years ago by J. J. Thomson¹⁹ as due to a process of *electron-transfer*, *e.g.* to the transfer of an electron from an atom of sodium to an atom of chlorine. The chemical affinity between sodium and chlorine was then attributed to the electrostatic attraction between oppositely charged atoms of the two elements.

In its most elementary form the new electrochemical theory was not very much in advance of that put forward a century before by Berzelius, since it gave no precise explanation to show why an atom of sodium should be ready to part with an electron or an atom of chlorine to accept one. Even in the hands of Ramsay,²⁰ therefore, it did not render any important help to chemists in solving the difficult problem of the nature of chemical affinity. When, however, we had

not only learnt from J. J. Thomson of the existence of the electron, and of its presence as a common constituent of all atoms, but had also been taught by Moseley how to count the electrons in the atom of each element, the situation was altered profoundly. Thus it was at once apparent that potassium with 19 electrons has only to lose a single electron, as J. J. Thomson had supposed, in order to acquire the stable grouping of 18 electrons which is characteristic of argon; and conversely, that chlorine with 17 electrons can acquire this stable configuration by gaining one electron. A motive for the transfer of an electron, and an explanation of the origin of this polar type of chemical affinity, can therefore be found in the exceptional stability of a group of 18 electrons, as contrasted with the relative instability of a grouping of 17 or 19 electrons, around a positively-charged nucleus.²¹ Indeed, only one important section of the problem now remains unsolved, namely, that we cannot explain why the properties of an inert gas should appear in successive members of the series

$$2 + 8 + 8 + 18 + 18 + 32 \text{ electrons,}$$

or what feature of the quantum theory dictates the formation of the sub-groups of 2, 3, 4, or 6 electrons, which by their summation give rise to the large groups of Rydberg's series:

$$2 \times 1^2 + 2 \times 2^2 + 2 \times 2^2 + 2 \times 3^2 + 2 \times 3^2 + 2 \times 4^2 \text{ electrons.}$$

Apart from this, the whole phenomenon of *electrovalence*, as Langmuir calls it, with its attendant theory of the complete and permanent ionisation of mineral salts such as Na^+F^- or K^+Cl^- , seems to be transparently clear.

Nevertheless, just as Berzelius' dualistic theory collapsed when faced with the facts of organic chemistry, so the theory of electron-transfer breaks down in face of the problem of explaining the mutual affinity of *like* elements. This is a serious fault, since the union of like atoms not only dominates the whole of carbon chemistry, but is also responsible for the formation of simple inorganic molecules such as H_2 , O_2 , N_2 , or Cl_2 . This second or 'non-polar' type of chemical affinity, however, has also received a clear explanation as a result of the study of atomic numbers. Thus it appears that two atoms, each of which is one electron short of the number required to produce the stable configuration of an inert gas, can acquire this configuration by a simple process of *electron sharing*.²² In this process a *duplet*, or pair of electrons, is held in common as an integral part of the electronic configurations of the two atoms which it unites, just as the two aromatic rings in naphthalene are united by the two carbon atoms which are common to both rings.

¹⁹ *Phil. Mag.*, 1904, **7**, p. 262.

²⁰ *J.C.S.*, 1908, **93**, 774.

²¹ See especially Kossel, *Ann. d. Phys.*, 1916, **49**, 229.

²² G. N. Lewis, *J.A.C.S.*, 1916, **38**, 762; "Valence," 1923, p. 74.

In this scheme of electron sharing there does not appear to be any *a priori* reason why two atoms should not be united by sharing *one* electron; and indeed Main-Smith²³ has postulated that this is a normal method of union in co-ordination compounds; but the evidence offered in support of this view is very slender and in general it appears to be a *pair* of electrons that performs this function, just as *pairs* of carbon atoms are shared when one six-atom ring is added to another on passing from benzene, C_6H_6 , to naphthalene, $C_{10}H_8$, and then to anthracene or phenanthrene, $C_{14}H_{10}$.

or

Two electrons held in common are therefore the equivalent of a *single bond*, or *covalence* as Langmuir calls it, whilst four or six electrons held in common give rise to a *double bond* and to a *triple bond* respectively.

The groups of eight electrons in the Rydberg series are generally depicted as occupying the eight corners of a cubical octet. A single bond is then represented by a pair of cubes with a common edge, and a double bond by a pair of cubes with a common face; but on this basis the formation of a triple bond would result in a complete superposition of the two cubes, and would thus give rise to a quadruple bond, with four pairs of electrons held in common instead of only three. The new model, therefore, fails to represent the property of forming single, double, and *triple* bonds (and the impossibility of forming a quadruple bond) which are expressed so well by the sharing of a corner, an edge and a face of the tetrahedra of le Bel and Van't Hoff. Indeed, further progress is possible only when we abandon the cubical model in favour of a purely algebraic form of the theory, or else adopt a different geometrical model, *e.g.* by supposing that the octet contains four tetrahedrally arranged duplets instead of eight equally distributed single electrons. This tetrahedral model enables us to see why, in the elements of the first short period, there is no large change of boiling-point on passing from $F-F$ to $O=O$ and $N\equiv N$; but when we come to carbon, where a quadruple bond between two atoms is impossible, the boiling-point suddenly rises by 3500° . This dramatic rise of boiling-point is obviously due to the fact that the spare bonds, which are left over after uniting the atoms in pairs by single, double, or triple bonds, interlock, until both

in diamond and in graphite the molecule extends to the boundary of the crystal, and vaporisation is only possible by disrupting atoms from this enormous molecular complex. If the cubic model were valid, this abrupt change should occur on passing from the double bond of oxygen to a prohibited triple bond in nitrogen, instead of on passing from the triple bond of nitrogen to a prohibited quadruple bond in carbon.

ORIGIN OF CHEMICAL AFFINITY.

By postulating alternative types of union, the electronic theory of valency enables us to recognise at a glance the existence of two types of chemical affinity, namely, a non-polar affinity between like atoms and a polar affinity between unlike atoms. It has the further advantage of referring both types of affinity to a common cause. This cause, long suspected to be electrical in origin, has at last been disclosed as depending on a mysterious force which compels the electrons, when under the influence of a positively-charged nucleus, to form stable aggregates of 2, 8, 18, or 32 electrons. The origin of these numbers, and of the sub-groups into which they can be further resolved, is, however, a secret which the quantum theory has not yet completely disclosed.²⁴

TWO THEORIES OF VALENCY.

During the last fifty years, organic chemists have accepted Van't Hoff's tetrahedron as a correct working model of the carbon atom. This conception of valency was vigorously attacked, however, in 1905, by Werner, who, in his "Neuere Anschauungen" (p. 73 of the English translation), asserted that "Affinity is an attractive force which acts from the centre of the atom and is of equal value at all points on its surface. With such a definition of affinity it naturally follows that separate units of affinity do not exist." In this paragraph, Werner challenges both the limited number and the fixed orientation of the four positions which are available for the attachment of other atoms in Van't Hoff's tetrahedral model. Bearing in mind the distortion of the tetrahedral angles, which is permitted by von Baeyer's 'strain theory,' Van't Hoff's model of the carbon atom can be represented most conveniently by a sphere with four sockets, each socket carrying an elastic rod to represent a bond by which the carbon atom is united to another atom. Werner's alternative conception can be represented most conveniently by Emil Fischer's model, in which the 'atom' takes the form of a sphere covered all over with bristles, a sort of spherical scrubbing-brush, which

²³ *Chem. and Ind.*, March 28, 1924, 43, 323.

²⁴ An interpretation of the periodic system, based upon the view that each planetary electron in the atom occupies a unique type of orbit characterised by four quantum numbers, has recently been described by Landé (*Die Naturwissenschaften*, July 1925, 13, 604); see also Sommerfeld (*Phys. Zeits.*, Jan. 1, 1925, 26, 70-74), and Pauli (*Zeits. f. Physik*, 1925, 31, 765-782).

resembles the involucre of a burdock in that two 'atoms' will stick together at any point of contact, and in any number up to the limits of space available.

Although Werner considered it necessary to denounce Van't Hoff's conception of valency as incompatible with his own more comprehensive views, it is now clear that these two theories are not in fact competing alternatives, since each is correct in its own domain, but incorrect if applied outside it. Thus Werner's theory of valency gives us an ideal representation of the behaviour of the closely packed ions in a crystal of rock-salt, and agrees precisely with the behaviour which we should expect of compounds which are held together only by *electrovalence*, i.e. by the mutual attraction of oppositely charged ions. It is, however, incapable of explaining the open lattice structure of the diamond, which can only be arrived at by limiting the number of points of attachment to four, and at the same time fixing their orientation around the atom, precisely as in Van't Hoff's model. This behaviour is characteristic of all compounds in which the atoms are held together by *covalence*, i.e. by the real *bonds* of the organic chemist. We therefore have alternative conceptions of valency, namely, Werner's theory, which expresses the type of chemical affinity that is dominant in mineral chemistry, and Van't Hoff's theory, which expresses the phenomena of organic chemistry; and we now find that these two theories correspond precisely with alternative aspects of the electronic theory of valency, which predicts the possibility, and compels us to recognise the real existence, of both types.

THE TWO TYPES OF VALENCY.

In general the two types of valency can be distinguished by merely counting the electrons. Thus, since the potassium ion and the chlorine ion have each a complete outer shell of eight *M*-electrons, we cannot replace the electrovalence by a covalence, since this would create a surplus of two electrons over and above those required to complete two stable 'argon' systems. On the other hand, a molecule of chlorine, with a total of only $2 \times 7 = 14$ *M*-electrons, must be held together by a covalence, i.e. by sharing two electrons, since if the atoms were torn apart we could only assign a complete octet of *M*-electrons to one atom, leaving the other with a sextet or incomplete group of six electrons. The conversion of the covalence into an electrovalence, as represented by the equation

may perhaps occur when the bond is broken by the rupture of the molecule when undergoing chemical change; but this ionisation of the bond can only give

rise to an unstable condition, which would always tend to revert to a more stable one in which each atom is able to complete its octet.

We can also distinguish the two types of valency by noticing that the 'polar' type of chemical affinity is indefinitely divisible, like Werner's uniform 'spheres of affinity,' but that the real bond of Van't Hoff's model cannot be divided. Thus in rock-salt the chemical affinity of each 'univalent' sodium atom appears to be divided equally amongst six 'univalent' atoms of chlorine and conversely; but in the diamond the four bonds of the 'quadrivalent' carbon atom are used as integers, each bond serving to unite two atoms, and two only. Whenever, therefore, mention is made of residual affinity, or of partial valencies, I at once suspect that these valencies must be *polar* rather than *non-polar* in character. This view was foreshadowed in 1899 by Thiele,²⁵ when formulating his new theory of *conjugation*, and I do not know of any evidence which would contradict it.

Even more important is the fact that, whilst an electrovalence can act in any direction round the atom, a real bond or covalence is fixed in direction. In the former case there is nothing to prevent the ions from being packed as tightly as their volumes will permit. This condition is realised in the crystal-structure of rock-salt, $\overset{+}{\text{Na}}\overset{-}{\text{Cl}}$, which is a close-packed aggregate of equal numbers of ions of opposite signs, and of fluorspar, $\overset{-}{\text{F}}\overset{+}{\text{Ca}}\overset{-}{\text{F}}$, where there are twice as many ions of one sign as of the other. On the other hand, the atoms of carbon in diamond are very far from being close packed, since each atom is surrounded immediately by only *four* other atoms, whereas each of Werner's spheres would be able to make contact with *twelve* other spheres of equal size. Indeed, it can easily be calculated that, if Werner's conception were correct in this particular case, and Van't Hoff's conception were wrong, the close packing of the spheres would increase the density of the crystal in the ratio of 3.5 to 8. Similar open lattices are found in many other crystals, and it is safe to assert that they can always be associated with the presence of valencies which are limited in number and fixed in direction, precisely as postulated by le Bel and Van't Hoff. Thus, if ice and quartz were mere aggregates of oppositely charged ions,

we should expect them to crystallise in the same form as fluorspar, where also there are twice as many ions of one sign as of the other. Actually, both ice and quartz crystallise in a totally different manner; and

²⁵ *Ann.*, 1899, 306, 87.

the lattice-work of ice is so open that the density of the aggregate is less than 1. We can therefore assert that the atoms of both compounds are united by real bonds and not by the mere electrostatic attraction between oppositely charged ions. A similar argument has already been applied in the case of iron pyrites, FeS_2 , where the sulphur atoms are all paired, instead of being distributed uniformly like the atoms of fluorine in fluorspar. The compound is therefore not a sulphide of quadrivalent iron $\overset{--}{\text{S}} \overset{++++}{\text{Fe}} \overset{--}{\text{S}}$; but a ferrous disulphide, $\overset{++}{\text{Fe}} \overset{--}{\text{S}} \text{---} \overset{--}{\text{S}}$, in which each pair of sulphur atoms is held together by a bond, in addition to carrying a double negative charge. It is, indeed, clear from these examples that the X-ray analysis of crystals provides a very precise experimental method for distinguishing between the two types of valency, and is of fundamental importance for this purpose.

POLAR, SEMI-POLAR, AND NON-POLAR DOUBLE BONDS.

Three years ago I pointed out²⁶ that since single bonds can be of two types, namely :

- (i) Polar, as in NaCl .
 - (ii) Non-polar, as in Cl-Cl , H-H or $\text{CH}_3 \cdot \text{CH}_3$;
- double bonds should be of three types, namely :

- (i) Polar, as in $\overset{++}{\text{Ca}} \overset{--}{\text{S}}$,
- (ii) Non-polar, as in O=O ,
- (iii) Mixed (or semi-polar), as in $\text{Me}_3\overset{+}{\text{N}}\text{---}\overset{-}{\text{O}}$.

In particular, a mixed or semi-polar double bond was postulated in trimethylamine oxide

and in the ions of oxy-acids²⁷

The existence of this new type of double bond has now been established by two independent experimental methods, depending respectively on the study of molecular volumes and on the detection of molecular dissymmetry. The work on molecular volumes, begun more than half a century ago by Kopp, has culminated in the recent researches of Sugden,²⁸ who has discovered a function of the molecular volume which is (i) independent of the temperature of observation, (ii) a strictly additive function of the constituent atomic volumes. In these investigations the molecular

volumes are reduced to *equal surface tensions*, by making use of a function $\gamma \frac{1}{4} \frac{M}{D-d}$ (where γ =surface tension, M =mol. wt., D =density of liquid, d =density of vapour), which Sugden describes as the *parachor*. The value of this function is increased by 23 units by each *non-polar* double bond, whatever the atoms which it joins, e.g. >C=O , >C=C< , >C=N- , -N=O ; but the *semi-polar* double bonds in the systems >SO , >NO and >PO were found to produce a minute *decrement* of molecular volume.²⁹ In this way the nitro group was shown to contain only one non-polar double bond, whilst the sulphinates, sulphonates, and sulphates do not contain any

More important still is the proof given by Phillips,³⁰ that the sulphinates (in which the existence of semi-polar double bonds was established by Sugden's measurements of density and surface tension) can be obtained in optically-active forms, as in the case of the ethyl tolylsulphinate of the formula

If the sulphur and oxygen were united by a symmetrical non-polar double bond, the compound would, on the basis of the older space formulæ, be obviously symmetrical. Moreover, since none of the earlier theories of valency was capable of predicting the asymmetry of these compounds, the experimental realisation of this new type of optical activity provides an excellent illustration of the value of the electronic theory of valency, as well as a decisive vindication of the more specialised conception of mixed or semi-polar double bonds. We have here, indeed, a further example of the general rule, already illustrated in the case of Werner's theory of co-ordination, that each new development of the theory of valency has been accompanied by, and has received its final sanction from, the discovery of a new kind of optical activity.

²⁶ J.C.S., 1923, 123, 822.

²⁷ Trans. Faraday Soc., 1923, 18, 285; Phil. Mag., 1923, 45, 1105.

²⁸ J.C.S., 1924, 128, 1177.

²⁹ Sugden, J.C.S., 1925, 127, 1525.

³⁰ J.C.S., 1925, 127.