

MODERN VIEWS ON VALENCY.¹

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LITERATURE ON VALENCY.

A DEPUTATION of your Association has told me that many school teachers find it a little difficult to get any considerable discussion of valency or the electronic formulæ of compounds in the ordinary text-books of chemistry. This applies to books like those of Newth, Alexander Smith, and Partington, which have been recommended from time to time for the Leaving Certificate course. There are, however, other books dealing more in detail with valency which can be recommended, such as Sidgwick: "The Electronic Conception of Valency" (Oxford University Press) and Butler: "The Chemical Elements and Their Compounds" (Macmillan). Besides these books there has been a great deal done in recent years to advance the subject of Valency. Sugden's book "The Parachor and Valency" (Routledge) would appeal to most teachers. Also the "Discussion on the Structure of Simple Molecules" at the British Association in 1931 is published with some other interesting discussions in a volume entitled "Chemistry at the Centenary (1931) Meeting of the British Association for the Advancement of Science" (Heffer & Sons, Cambridge, 1932).

In this latter volume there is a paper by Professor R. H. Fowler which shows what a change has taken place in the idea of valency as held by physicists.

While in the past valency has been found a useful convention by chemists—an indispensable convention required for the writing of chemical formulæ—physicists have not troubled themselves to take any special interest in valency.

However, let us see what Fowler says. "Quantum mechanics has recently developed in such a way that it provides a natural explanation of valency. One may say now that the chemical theory of valency is no longer an independent theory in a category unrelated to general physical theory, but just a part—one of the most gloriously beautiful parts—of a simple self-consistent whole, that is, of non-relativistic quantum mechanics."

¹ An address given to the Science Teachers' Association on 14th August, 1933, at the University of Sydney.

The sources of information on valency already given above will probably suffice for most of you, but should any desire to look into the matter more deeply, the following references are given. (I am indebted to my colleague, Dr. J. E. Mills, for these references.)

- Pauling, *Jour. Amer. Chem. Soc.*, **53**, 1367 and 3225 (1931).
,, *Jour. Amer. Chem. Soc.*, **54**, 988 (1932).
,, *Proc. Nat. Acad. Sci.*, **18**, No. 4 (1932).
G. N. Lewis, *Jour. Chem. Physics*, Vol. I, 1933.
Mulliken, *Phys. Review*, **40**, 55 (1932).
,, *Phys. Review*, **41**, 49 and 751 (1932).
,, *Chem. Reviews*, **9**, 1931.

THE VALENCY BOND IN CHEMICAL FORMULÆ.

Kekulé was one of the first chemists to express the idea of valency in his symbols of the elements (1859), but his notation did not come into general use. Accustomed as we are to modern notation showing bonds (lines or dots), it is hard to realize that this system has only been used since 1865 (Crum Brown). Little change has been made in the methods of writing graphic formulæ since then. There are now conventions in organic chemistry with regard to the lettering of the atoms in open chains and in cyclic compounds. There is also the occasional use of a roman numeral above the symbol of an element in compounds to indicate its valency when the valency of the element is a variable one, *e.g.*, Cu^{II}, Pt^{IV}. Graphic formulæ are, on the whole, satisfactory and, as judged by results, have been most useful.

POLAR AND NON-POLAR VALENCY.

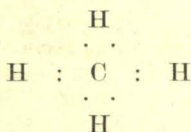
Professor Gilbert Lewis of California brought out his book on Valence in 1923 (Chemical Catalog Co.). He put forward the idea, which he had already published in journals, that one ordinary valency bond may be interpreted as being the sharing of two electrons by adjacent atoms (non-polar valency), while in electrolytes (polar valency) the valency of an atom (or group) can be taken as the number of electrons which it gives up to or accepts from another atom. This idea has stood the test of trial for at least a decade, and has been found in the main to be satisfactory. The two "bonding" electrons in a covalent linkage (single bond) come from the highest energy level (outermost shell) of the two atoms, one electron from each atom. However, in elements of variable valency, such as copper, electrons for binding may come also from a lower

level. Sugden finds that a single bond between two atoms may occasionally be represented best by a single electron coming from one of the atoms concerned. In homo-polar (non-polar) valency a double bond is represented by four electrons held in common between the two atoms. In polar valency a double bond means the giving up of two electrons from one atom to another atom (or group). One usually tries so to adjust the number of electrons that there are eight of these in the highest energy level of each atom in a compound. It is not always possible to get eight, but if not eight, one tries to get twelve, or six, or at least some other even number.

Lewis suggested in his book that the eight corners of a cube could be used to represent the electrons in the highest energy level of the atom. But the cube is not now much used in the representation of atoms or of the combination between atoms. The tetrahedron and the octahedron are more often used to represent atoms. An atom can also be represented by a sphere or by a circle, the projection of a sphere. This method of representing the atom is probably the most generally useful. The size of the circle is known in compounds with polar valency. In the positive and negative ions of these compounds the atomic "spheres" are considered to touch, but not penetrate or overlap. In the compounds with non-polar valency the distance between the centres of the atoms, taken along with the rate at which the electron density falls away from the centre of each atom, indicates that there is a certain amount of overlap of the domains of the atoms. [See W. L. Bragg, *Nature*, 128, 210 (1931).]

It is convenient in compounds with non-polar valency to represent the circles (atoms) as cutting (overlapping) one another. The electrons in the outermost shell are represented either by dots or, better, by a small letter indicating the atom from which the electron is derived; for example, methane, CH_4 , may be represented as in Fig. I.

Most chemical books, however, represent the symbols without surrounding circles, and use dots for the electrons thus:



In the representation of a double bond (non-polar) it is usual to employ the device $\text{C}::\text{C}$ rather than $\text{C} \ddot{\text{C}}$. This practice is misleading in so far as it suggests that the

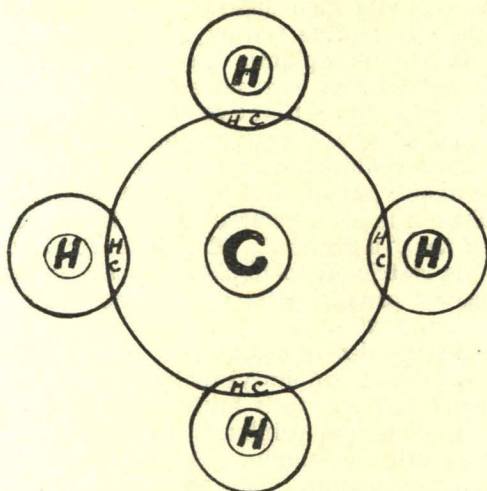


Figure I.

centres of the carbon atoms are further apart in a double bond than when connected by a single bond $C : C$, because the reverse is the case. I have always preferred to write a double bond with the four electrons in the common overlapping region of the two circles, the centres of the circles being closer together than with single bonds.

While this method of representing the combination of atoms is useful, it is perhaps hardly necessary to state that the fixing down of the electrons in definite positions is theoretically indefensible.

The electrons are not fixed. Indeed, even the idea of a series of electron orbits is being replaced by a wave-mechanical distribution which cannot be visualized. In spite of this I would recommend that the methods adopted by chemists to represent the electrons in the outermost shell of the atoms, and the use of these electrons in binding together the atoms, be continued. They are most helpful, especially in writing down the formulæ of addition and co-ordination compounds. Their use has helped in preparing many new compounds and has explained cases of isomerism which could not otherwise have been explained.

SEMI-POLAR BONDS.

Semi-polar bonds are another type of valency which has to be assumed in the case of substances like orthophosphoric acid, perchloric acid, sulphuric acid, and their salts. It is also assumed in substances like sulphuryl

chloride (SO_2Cl_2) and phosphorus oxychloride (POCl_3). In phosphorus oxychloride the oxygen atom is supposed to be held to the phosphorus atom by two electrons contributed (only) from the phosphorus atom. If, in this union, it were assumed that two of the oxygen electrons were also contributed to the overlapping region, then the phosphorus atom would have ten electrons; but, wherever possible, one avoids attributing ten electrons to an atom. Sugden confirms the semi-polar bond in this case by his calculation of the "parachor." The determination of the "parachor" is restricted to liquids, but the constitution of a substance not usually in the liquid condition can often be inferred from that of a substance whose parachor is capable of being determined. For example, thionyl chloride (SOCl_2) and sulphuryl chloride (SO_2Cl_2) have semi-polar bonds, so one feels fairly certain in assuming that sulphur dioxide and sulphur trioxide should also be written down with the sulphur electrons alone holding the oxygen to the sulphur. This means that the sulphur atom is assumed to have six electrons (only) in its highest energy level. The ions CO_3^- , NO_3^- are known to have the three oxygen atoms all in exactly the same relation to the central atom (C or N). Here also one assumes that no oxygen electrons are made use of when carbon is bound to oxygen, or nitrogen to oxygen in carbonates or nitrates. Sugden's phrase *semi-polar bonds* seems likely to remain.

With regard to co-ordinate linkages, Sidgwick suggested originally that these are of the same type as that just indicated for the semi-polar bonds. For example, in tetrammine cupric sulphate, $[\text{Cu}^{\text{II}}(\text{NH}_3)_4]^{++}[\text{SO}_4]^{--}$, it is possible to conceive of this compound as having each of the four ammonia groups holding on to the copper atom by means of two of the nitrogen electrons. This would make the compound semi-polar. I agree with this view, which may be called Sidgwick's view. Sugden suggests that in some of these co-ordination compounds between ammonia and a central metal atom each ammonia molecule is attached to the metal by only one (nitrogen) electron. Others suggest that the ammonia molecules just touch the copper atom and are held to it by a measure of "electrostatic" force. According to this last view the positive copper ion attracts the slightly negative nitrogen atom, whereas on the Sidgwick view the nitrogen atoms are given a certain amount of positive polarity by the combination. One inclines to support the Sidgwick view because of the very great stability conferred on a central atom (*e.g.*, Cu^+ or Cu^{++}) in some of the co-ordination compounds prepared and described by G. T. Morgan and his colleagues.

(See the Journal of the Chemical Society for the last ten years.)

CONSTRAINT IN THE MOLECULE.

In non-polar valency we may sometimes have a state of *constraint*. This is noticeable in the case of organic substances which have double bonds. The distance between the centres of two carbon atoms connected by a single bond is 1.54 Ångstrom units, whereas in the case of a double bond it is 1.38Å. This drawing together of two carbon atoms by a double bond affects the properties of the other atoms in such compounds. For example,

allyl bromide, $\overset{1}{\text{C}}\text{H}_2=\overset{2}{\text{C}}\text{H}-\overset{3}{\text{C}}\text{H}_2\text{Br}$, has a more reactive

halogen atom than vinyl bromide, $\overset{1}{\text{C}}\text{H}_2=\overset{2}{\text{C}}\text{HBr}$. The carbon atoms Nos. 1 and 2 being drawn closer together than Nos. 2 and 3, the halogen atom on No. 2 atom is held more tightly than the halogen atom on No. 3 atom.

The effect of a strain can sometimes be propagated, from atom to atom, a considerable distance. This is, for instance, at least part of the explanation of the way in which the diderivatives of benzene are formed from the monoderivatives. (*Journal of Chemical Society*, 1930, page 2358.) The carbon atom is only very slightly negative in character when alone or combined with hydrogen. But under certain conditions it becomes more negative and so, according to R. Robinson, more reactive. A negative (key) atom somewhere in a molecule can render the neighbouring (carbon) atom somewhat positive. The next carbon atom again will be slightly negative. This kind of impulse is transmitted the more readily when there are alternate single and double bonds, as we have them for instance in the benzene molecule. Consider that benzene has had one of its hydrogen atoms replaced by a nitro group to form nitrobenzene. In this compound, $\text{C}_6\text{H}_5\text{NO}_2$, oxygen is the most negative element, and may be looked upon as the key element. It transmits an influence of alternate polarity through to the benzene ring, rendering the carbon in the meta position negative. This is the essential condition for reactivity of the atom, and the diderivative here is always a meta-derivative. In the compound $\text{C}_2\text{H}_5\text{NH}_2$, nitrogen is the most negative (key) atom, and renders the o- and p- positions in the ring negative, so that it is in these positions we expect to get action when forming a diderivative from aniline.

It will be seen from these suggestions that the whole subject of the structure of the atoms in molecules is of

great interest. The exact positions of the atoms in larger numbers of molecules are now being obtained by X-ray measurements, and light is also being thrown on the exact nature of the bonding by the examination of the Raman Spectra and other methods.

One feels that in a few years we shall understand the meaning of valency in fuller measure.

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