THE ELECTRONIC THEORY OF VALENCY*

THE remark of Sir J. J. Thomson while opening a discussion on the subject at the Faraday Society in 1923, "The electron dominates the field of chemistry", is true even now, though our approach to the problems are somewhat different to-day. A satisfactory theory has to take into account not only the possible stable molecular forms but also the means of attaining the requisite configuration while ordinarily valence theory takes note of only the former.

The electronic theory of valency begins with the publications of Lewis and of Kossel and using a static model of the atom Lewis was able to explain a whole lot of chemical facts. By the time these were reconciled with the dynamic model of Rutherford and Bohr with Lewis's postulate, "an orbit as a whole, and not the electron in some one position within the orbit, is the building stone of atomic and molecular structure" one had to reckon with the upheaval caused by the new quantum theory. Chemists have been accustomed to classify bonds into various types: ionic, homopolar, semipolar and metallic, in the interpretation of each of which the quantum theory has been used. The present report deals with this new development. These classifications can be regarded at best as a useful guiding principle, the concept of valency itself being essentially vague. The concept and the classification can best be regarded as a convenient simple picture of the fundamental energy relationships on which molecular architecture is based.

In tackling the problem of molecule building with known atomic structural units, the principal difficulty facing the investigator has been mathematical and approximations were, therefore, inevitable. We have two different modes of approach: the method of molecular orbitals developed essentially by Lennard Jones, Hund and Mulliken and the method of localised electron-pairs or the H-L-S-P method. Lewis's concept of the ionic bond is essentially valid even now while the interpretation of the metallic bond is a triumph of the new quantum theory but the covalent or homopolar bond is the one that has brought out the limitations of either method of approach.

When atoms are brought together, the interatomic interactions may be expected to appreciably modify the atomic wave functions but as a first approximation, one can treat these as remaining unchanged. This assumption is implicit in both the methods. The energy of a molecule can be expressed as a sum of Coulomb integrals involving atomic wave functions and exchange integrals involving electrostatic interactions of electrons and nuclei. In choosing the atomic wave functions, the ground state is not the only one to be considered. For instance, in the formation of hydrogen from the atoms, kinetic studies have shown that the formation of the molecule involves a three body collision in which the third body takes away the excess energy liberated in the reaction. In interpreting the interaction one has to visualise a non-classical effect whereby a strong attraction is followed by a repulsion, an equilibrium corresponding to molecule formation being obtained. For a stable bond between the atoms, the two electrons taking part must combine so that the resultant spin becomes zero, the bond energy being the sum of the two types mentioned earlier. The initial success of the Heitler-London method with hydrogen led to a rapid though incomplete development of the theory to the interaction of atoms with several electrons with more than one unpaired. In these applications, one has often to consider excited states of the atom in addition to the ground state. Combining these ideas with a consideration of electron density distribution in space, Pauling and Slater have devised a theory of directed valence forces consistent with the known stereo-chemistry of carbon compounds.

A normal carbon atom has the arrangement of electrons $1s^2$, $2s^2$, $2p^2$ and the normal state is $^3P_0$ with the slightly higher ^1S and ^1D. Assuming the wave functions of an electron to be separable and factorised into radial and orientational factors, the $2p$ electrons must differ in their orientational part. With two such unpaired electrons, two stable bond pairs can be formed. Four bonds can, however, be formed by the excited ^5S state of carbon with the configuration $1s^2$, $2s^1$, $2p^3$. In all cases where bond energy exceeds a value of 1·6 volts (the difference between the two states of carbon), one can reasonably assume the participation of this state and most organic compounds happen to belong to this category. Using the ^3P and ^1D states it is possible to construct a divalent carbon atom, but a tetravalent carbon atom requires four electrons, each independent and in a singly occupied orbit. An sp^3 configuration enables the construction of four independent orbits. Three mutually perpendicular p electrons and a spherically distributed s electron with the mutual repulsive forces of the hydrogen nuclei can lead to a tetrahedral form for the methane molecule, but this would imply one carbon-hydrogen bond different from others, which is contrary to known experimental evidence. Now any suitable wave function must satisfy the conditions that the orbits must be mutually orthological and have the aggregate configuration $2s2p^3$. Pauling has shown that both these and the equivalence of the C-H bonds in methane, satisfied by using the concept of sp hybridisation. *The use of hybrid bond orbital functions is an essentially empirical approach* that has been justified by its successful interpretation of phenomena in organic and inorganic chemistry. This hybridisation, by introducing the $2s$ wave functions in the compound orbital functions is considered possible only if the energy of the $2s$ state is not very different from that of the $2p$.

Mention should be made at this stage of a fundamental principle of quantum mechanics used in chemical applications and underlying

the concept of 'resonance'. Any structure representing a system corresponds to a wave function ψ and the energy value calculated using the correct wave function ψ_0 is lower than that calculated using any other wave function ψ. If there are several structures that might conceivably represent the normal state of the system, a general function of the form

$$\psi = a\,\psi_1 + b\,\psi_{11} + c\,\psi_{111} + \cdots\cdots + n\,\psi_N$$

can be obtained. The best relative values of the coefficients are obtained by making the energy value a minimum. The structure of such a system is *not intermediate between the various forms* but the normal state is described as *involving all structures in resonance*. As a consequence of this, the system is stabilised by an amount of energy, 'the resonance energy'. There is a certain amount of arbitrariness in the concept of resonance but this is to some extent offset by the convenience and value in its chemical applications.

The concept of resonance is common to both methods of treating valence problems. In the HLSP method, the contribution of ionic terms corresponding to both the electrons being with the same nucleus is not given adequate emphasis and the expression for the total energy of a system does not take into account the effects due to the Pauli exclusion principle. In the method of molecular orbitals both these are taken note of with a possible overemphasis of ionic terms. The wave function expresses the motion of an electron in the resultant field from all the nuclei and the other electrons in the system. For a diatomic molecule the theory is essentially a discussion of the quantum numbers of electrons in an axially symmetrical field. Mulliken observed that extension to a polyatomic system resolves itself into a question of determining the behaviour of various atomic orbitals conforming to the symmetry of the system.

The position is analogous to conditions pertaining to the movement of an ion in the field of other ions. While it is difficult to say categorically whether the method of molecular orbitals or the HLSP method is the better approximation, the molecular orbital methods are more convenient for qualitative discussion but the HLSP method has been more often used for quantitative calculations.

Among the useful results obtained by Pauling's interpretation of the chemical bond, bond energy, bond length, bond order and partial ionic character of covalent bonds constitute a fundamental departure from earlier approaches to the subject. The method has been remarkably successful in the study of organic compounds but one has to guard against an overemphasis of the findings of such analysis. Both the electronegativity scale and bond energy relationships are essentially empirical. In deriving bond energy values, Pauling uses the postulate of the additivity of normal covalent bonds and where this fails, the postulate of the geometrc mean. Pauling himself remarks, "It is probable that in general, the postulate of the geometric mean leads to somewhat more satisfactory values than the postulate of additivity for normal covalent bonds between unlike atoms, ... We shall find it

convenient to make some use of the postulate of additivity as well as the postulate of the geometric mean" (*italics mine*). From single bond energy values determined by an analysis of thermochemical data complete electronegativity scale has been built up, and in a very large number of cases the values thus obtained are proportional to the sum of the first ionisation energy and the electron affinity of the atom. Where atoms are linked together by single bonds, the bond moments are found to be related to the difference in their electronegativities. There are, however, significant exceptions. On the basis of the electronegativity scale the carbon-iodine bond cannot have any significant amount of ionic character, and hence should have zero moment, but is found to have the same bond moment as other carbon-halogen bonds. The phosphorus-hydrogen bond is another instance where the correlation breaks down. With such exceptions, one has to view with some circumspection conclusions on the partial covalent character of bonds in ionic crystals, unless some more unequivocal evidence is forthcoming.

The correlation of bond distance and bond order is on a somewhat better footing. If the potential function of the resonating bond be represented as the sum of two parabolic functions involving the single and double bond potential functions, an expression of the type

$$V(R) = \tfrac{1}{2}(l-x)\,k_1(R-R_1)^2 + \tfrac{1}{2}\,x\,k_2(R-R_2)^2$$

is obtained. The derivative of this with respect to R equated to zero for the equilibrium order and the force constants. If k_2/k_1 is taken as 3, one gets

$$R = R_1 - (R_1 - R_2)\frac{3x}{2x+1}$$

The curve corresponding to this equation agrees very well with the experimental values for carbon-carbon bonds and with a change of scale for other bonds as well. The force constant ratio, however, is more than that of any known instance and Pauling attributes this discrepancy to the neglect of resonance energy in the assumed potential function. Using the observed constancy in the carbon-carbon single-bond distance in the saturated hydrocarbons and in diamond, this concept of bond order has enabled the interpretation of conjugated systems and the phenomenon of hyperconjugation.

The concept of resonance has also been used in the interpretation of the aromatic compounds and their reactivity together with a plausible explanation for the existence and stability of free radicals. Another important application of these concepts is provided by structures involving hydrogen bonds without the necessity of postulating a covalency of two for hydrogen.

An important extension of the same principles of hybrid bond orbital functions is in the interpretation of the complex compounds of the transition elements. Notable examples are provided by the metal carbonyls, and the cyanide complexes in which the metal carbon bonds are much shorter than could be accounted for with a single bond while the carbon-oxygen and carbon-nitrogen bonds turn out to be longer than required by a triple bond.

Mention should be made here of the different significance to be attached to the term 'co-ordination'. The classical chemical concept couples this with the donor-acceptor properties of atoms or ions. In the interpretation of ionic crystals and in the metal complexes we notice a different meaning. As with other bonds, co-ordination also involves both co-valent and ionic types.

A logical extension of the resonance concept is the interpretation of the transition-complex in a chemical transformation as a system in which the extreme degenerate structures are the reactants and the products. Polanyi and co-workers have been able to successfully interpret the substitution reactions of alkyl halides on this concept and one may naturally expect more developments on these lines.

In the discussion that followed, Sir C. V. Raman drew attention to the observations of Mr. G. N. Ramachandran on the fluorescence spectrum of the diamond which appeared to go against the whole concept of hybridisation as interpretation of the results was possible by assuming the existence of carbon atoms in the ground state alone in the diamond molecule. Against this it was pointed out that the mass of chemical facts that required the concept for a proper interpretation and the possibility of the selection rules having to be different with hybrid bonds could account for any apparent discrepancy.

Dr. Nagendra Nath gave an ingenious picture of bond formation between carbon atoms (*single bonds only*) without any hybridisation involving the $2s$ electrons of one atom and the $2p$ electrons of the other by an extension of the Hietler-London treatment of hydrogen molecule. In order to satisfy the requirements of spin, it was assumed that the paired electrons got unpaired before bond formation. Using this picture he was able to account for the four forms of diamond. In the course of the discussion, Dr. Nagendra Nath said that no attempt has been made by him to interpret multiple bonds nor the case of bonds between different atoms. Even with regard to the particular bond in question one has to await fuller details before accepting or rejecting the interpretation.

Dr. G. V. L. N. Murti gave a brief account of the application of Raman spectra to interpret hydrogen bonding. Prof. K. S. Krishnan, the Chairman of the Symposium, Prof. Bhagavantam and others took part in the lively discussion that followed.

S. V. Ananthakrishnan.

CHEMISTRY AND PHARMACY*

IN the course of his Presidential Address to the Sixth Session of the All-India Pharmaceutical Conference held in Bangalore during the first week of January 1946, Sir S. S. Bhatnagar said :—

"A nation that merely follows the example of other nations, howsoever great it may become, can never lead. Industry will really flourish only in those countries' which are able to produce quality goods of an original character. We should, therefore, cease to quarrel over trivial issues such as the relative importance of pure and applied sciences and get to brass tacks, particularly as there is no line of demarcation between the two so far as your own science is concerned. Not long ago, chemistry was entirely pharmacy and pharmaceutical chemistry, and all chemists of any note were really pharmaceutical chemists. The interesting fact is that in your domain, it was the applied science that gave birth to the science of pure chemistry. With the rapid growth of pure science, the relative importance of the two may have changed. Nevertheless, the fact remains that pure chemistry is a child of pharmaceutical chemistry and howsoever much the pure chemist may look down upon a pharmacist or a pharmaceutical chemist, he has to admit that pharmaceutical chemistry provided him with excellent ancestry. The most recent achievements of the chemist which have resulted in the development of such medicinal substances as penicillin, D.D.T., streptomycin, gammexane and several new sulpha drugs seem to show that pharmaceutical chemistry experienced a specially virulent growth during the fateful years of this war. Nobody connected with researches on these important subjects can be branded as a mere druggist and assigned to a lower order of scientific achievement. However, in order to raise your status in international science, the pharmaceutical chemists and the pharmacologists and the medical men amongst you, must concentrate on high class research work. That India has the necessary talent to make contributions of great importance in these subjects can be gathered from the fact that several outstanding discoveries have been made in the past in this country. For example, after the brilliant discovery of Chistina and Caronia that tartar emetic was useful in the treatment of infantile kala-azar of the Mediterranean basin, Rogers in India introduced the use of tartar emetic intravenous for the treatment of Indian kala-azar. Soon after this, Sir U. N. Brahmachari introduced the use of sodium antimonyl tartarate for the treatment of the disease; subsequently his name as the discoverer of urea stibamine, a cure for kala-azar, became well known far and wide, as this drug above all others has helped greatly in the conquest of kala-azar in India. The drug industry which followed in the wake of Sir U. N. Brahmachari's discovery, is India's very own and will long remain hers as both the discovery of the cure and manufacture of urea stibamine were results of indigenous talent. Mention must also be made here of researches carried out by

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