



Fig. 4.

From among the many innovations embodied in the NEOPHOT, mention must be made of the remote control of the coarse and fine motions by means of two shafts, one on either side of the optical bench. These always remain in a fixed position and permit of convenient manipulation of the focussing motions from any standpoint beside the camera. A great deal of favourable comment is accorded by users to the anti-vibration mounting and to the swivelling filament lamp for visual examination in bright field which is attached to a screen designed to exclude stray light and saves the need for using the Arc Lamp for visual observation. The anti-vibration mounting functions dependably even in locations subject to severe vibrations.

The equipment for general survey photography

with vertical illumination, by means of a plane glass and illuminating lens, can be easily exchanged for a sliding mirror and swivelling ground-glass which provide oblique illumination for the macrophotography of irregularly shaped objects.

Figure 4 shows the equipment for macrophotography of large objects. The object stage and illuminating mirror are simply swung into or out of position as needed. The microscope stand need not be removed; screwing up the object stage in order to permit the rays to pass from the lamp to the mirror, is all that is required.

As has been experienced so far the NEOPHOT not only satisfies all demands relative to serial metallurgical and other industrial examinations but also represents the ideal and perfect apparatus for research.

## Band Spectra and Valency—II.

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### TWO POSSIBLE THEORIES OF VALENCY.

Both the theoretical bonding effects being always present a selection between the two postulates amounts to a choice as to which of these two effects is the more predominating. This involves considerations regarding the dissociation process and the dissociation energy, and therefore the method of molecular orbitals *per se* is not able to decide this question. It can be shown, however, that to reduce the phenomenon of chemical linkage to that of non-promotion is not justified already in the interpretation of the excited terms of  $H_2^+$  all of which are unstable (with the exception of the promoted  $3d\sigma(2p)$  which has a minimum at large internuclear distance) no matter, whether the electron is on a promoted orbital or on an unpromoted one. This appears significant, because the single bond interpretation of the method of molecular orbitals is a generalisation of the conditions in the molecule  $H_2^+$ .

The differences of the two conceptions are rather far reaching. They concern particularly

the counting of valencies and the conceptions of chemical union itself. The first one we may discuss by taking up the case of the molecule CO. The electronic configuration of its ground-level contains six  $p$ -electrons, on which the linkage rests in any case and which form in the molecule the groups  $\pi^4(2p)$  and  $\sigma^2(2p)$ . Both orbitals are non-promoted and according to the single electron bond interpretation in which the number of valencies equals the number of non-promoted pairs *minus* that of the promoted ones, those six electrons represent a triple link. According to the pair bond interpretation only those pairs contribute to the linkage, which are composed of electrons of either atom. The C atom possesses only two  $p$ -electrons and therefore only two out of the three pairs contribute to the linkage, the two remaining electrons of oxygen do not take part in it. The same configuration  $\pi^4(2p)\sigma^2(2p)$  occurs again in  $N_2$  but here also the pair bond interpretation recognises a triple bond, because each of the partners contributes three electrons. This distinction is by



no means superfluous, because only when in cases like CO the second way of counting the valencies (Hund's counting) is valid, the maximal valency of any atom equals the number of its outside electrons and a simple and uniform chemical theory of valency is possible, otherwise this simple relation is lost and we are forced to introduce a large number of hypotheses in order to interpret the experimental results of chemistry.

The second consideration concerns in the main, polyatomic molecules. In the interpretation of the orbital method as a pair bond theory the interaction of the electrons produces electron pairs, which link two atoms, and are localised between them. Because this interaction is missing in the single electron bond interpretation, in polyatomic molecules the electrons are not localised, and do not belong to any two particular nuclei but are related to all nuclei of the molecule. But this view leads automatically to wrong statements on the dissociation processes of the biggest class of molecules. If the electrons are treated as independent, we obtain *e.g.*, in  $H_2$  as dissociation products 50% neutral atoms  $H + H$  and 50% ions  $H^+ + H^-$ . In  $CH_4$  we obtain even 27% neutral atoms only and 73% of the molecules must be assumed to dissociate into various ions. If the electrons would be independent in  $H_2$ , then indeed the probability of either electron, to go with one or the other of the nuclei would always be 50%, no matter whether the other electron is already in the vicinity of this nucleus or not. Hence the "overionisation" of the non-localised wavefunctions is a direct expression of the neglect of the interaction inside the electron pairs. The choice of an electron of  $H_2$  to go with a particular nucleus will, however, depend on the choice of the other electron too, when their interaction is introduced and only then the theory gives a correct statement on the process of dissociation or formation. Nevertheless, some

localised between two atoms each. Indeed, some kind of interaction must exist between *all* the electrons of a molecule, or, in other words, any electron will belong to any nucleus with some probability, but the orbital method without considering the actual process of formation, is not able to find out the strength of the different interactions. The result of that localisation which obtains the correct dissociation products, may be described by a strong interaction inside each electron pair and weak interaction from pair to pair. This is the type of strong localisation, which appears to exist in all molecules of the first order.<sup>7</sup> But the type of molecules with non-localised electrons exists too. The benzene ring doubtless possesses non-localised electrons and because they do not belong to particular nuclei, all the structural formulæ proposed by chemistry, are true at the same time. This explains the particular behaviour of cyclic compounds, but because this behaviour is different from that of normal molecules of first order, it indicates also, that the bonds of the latter ones are produced differently, *i.e.*, by electron pairs. A second type of non-localised bonds probably exists among Werner's molecules of second order, *i.e.*, among genuine complex salts<sup>8</sup>.

Thus we see that both theories of valency are justified in their own domain. It appears, as if in the discussions of recent years, the distinction between the two possible wavemechanical treatments and the two possible theories of valency has been lost sight of at a too early stage, thus causing some misunderstanding. The two mathematical treatments are certainly both correct, the H.L.S.P. method more adapted for large and the orbital method more for small internuclear distances. The two theories of valency describe each correctly certain different types of molecules. But because both the wavemechanical treatments yield a theory of valency only by the

	Wavemechanical Method	Valency Theory	Author of this combination	Remarks
1	H. L. S. P.	Electron Pair Bond	Heitler and London, Slater, Pauling.	
2	H. L. S. P.	Single Electron Bond	Pauling and Collabort. (Ring Structures)	Non-Localisation by Hybridisation of different Structures.
3	Orbital	Single Electron Bond	Mulliken (General Theory of Valency). Hund (Molecules with identical nuclei).	Unpromoted Electrons obtain Attractive $U : r$ curve. Over-ionisation.
4	Orbital	Electron Pair Bond	Hund (Molecules made up of different Atoms. Crystals) Present paper. (General Theory of Valency for Non-Aromatic Molecules of first order.)	Electron Pairs obtain attractive $U : r$ curve.

authors have preferred the description of the molecule by non-localised wavefunctions, because it appeared, as if the localised functions, as given at first by Hund, represent a poorer mathematical approximation. It could, however, be shown recently, that a different procedure by reducing the ionic terms is always possible, which gives the correct products of dissociation and wavefunctions which are strongly, but not completely,

introduction of a postulate, both can be combined with either of the two valency theories. As a matter of fact, all the four possible combinations

<sup>7</sup> H. Lessheim and R. Samuel, *Rev.* (1), page 636 ff.

<sup>8</sup> The non localisation of the bonds is probably also more or less realised in certain polyatomic hydrides, which approach the view-point of the united atom on account of their small internuclear distances.



can be found in literature and it may not be out of the way, to give an example for each of them in the above table.

#### SOME ARGUMENTS FOR THE PAIR BOND THEORY.

Because the wavemechanical method becomes a theory of valency only by the introduction of a postulate in whichever way it may be introduced (*e.g.*, by the fixing of the energy relation of the left- and right-hand side of the correlation table or the reduction of the ionic terms, etc.), the decision can be obtained not from the mathematical treatment itself, but only by comparing the consequences with the experimental facts. To our mind the results obtained during the last two or three years clearly indicate, that the description of molecules of the first order (as distinct from organic ring structures or genuine complex salts) by a uniform pair bond theory of valency is a closer approach to reality, even if it involves the sacrifice of the Octet Theory or of co-ordinate linkages in this most important class of molecules. Some of the reasons, which lead us to this point of view, may be summarised as follows:—

(1) The value of the dissociation energy of  $\text{LiH}$ , the non-existence of  $\text{LiH}^+$ ,  $\text{Li}_2^+$  and  $\text{BeH}^{2+}$  etc. together with the existence of  $\text{LiH}$ ,  $\text{Li}_2$ ,  $\text{BeH}^+$  and  $\text{BeH}$  indicate, that the bonding effect of the single electron on account of the degeneracy of the atomic fields is very weak. It becomes appreciable only in  $\text{H}_2^+$ , where the fields are rigorously degenerated and the internuclear distance is small.

(2) The excited terms of  $\text{H}_2^+$ , in which the electron is non-promoted, *i.e.*, bonding, are all repulsive.

(3) The interaction of the electrons is the decisive bonding effect in the H.L.S.P. method. It cannot be neglected in the orbital method because it is just that part of the interaction, which cannot be replaced by a simple screening effect, that the symmetry relations of the total wavefunction depend upon.

(4) If the interaction inside the electron pairs is neglected, the wavefunctions are "over-ionised" and the orbital method gives quite incorrect results as to the products of dissociation. The ionic terms are a direct representation of the independence of the electrons.

(5) Two unpromoted electrons, which form already a closed group in the separated atom, act anti-bonding, and not bonding. This is shown by the band spectra of molecules of the type  $\text{BeO}$ ,  $\text{BeF}$ , and  $\text{AlO}$  where the  $2s^2$  group acts repulsively.<sup>3,6</sup>

(6) On the other hand, the excitation of a single unpaired electron, like in  $\text{SiF}$ ,  $\text{NO}$  or  $\text{BeF}$ , produces an increase of the energy of formation.<sup>2,6</sup> Considerations 5 and 6 appear to be definitely confirmed by the band spectra of a large number of molecules and particularly by that of  $\text{CdF}$ . Here the first term difference of  $\text{Cd}$  is much higher than that for a metal of the main group of the periodic table and it is therefore impossible to correlate the ground state of the molecule to the ground state of the  $\text{Cd}$  atom.<sup>3</sup>

(7) In the single electron bond interpretation the energy of dissociation should go parallel with the polarity of the molecules, because the degeneracy of the atomic fields produces not only the polarity but at the same time the bonding effect. But throughout the periodic table the energy of dissociation goes with the field strength,

regardless of the polarity. In the series  $\text{CO}$  to  $\text{PbO}$  it decreases with increasing polarity, from  $\text{CO}$  to  $\text{CS}$  and  $\text{CSe}$  it decreases with decreasing polarity.

(8) The amazingly high energy of adiabatic dissociation of  $\text{CO}_2$ , as revealed by the analysis of the infra red spectrum, indicates, that it is formed by a  $\text{C}$  atom with 4 equivalent  $p$ -electrons.<sup>7</sup>

(9) The bond energies of the chlorides and oxychlorides of sulphur as measured by the absorption spectrum of the vapours, indicate, that the  $\text{S-Cl}$  bond in  $\text{SCl}_2$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{SOCl}_2$ , the  $\text{S=O}$  bond in  $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{SOCl}_2$ , the  $\text{S=S}$  bond in  $\text{S}_2$  and  $\text{S}_2\text{Cl}_2$  possess practically the same strength. This contradicts those formulæ, in which the bond is sometimes supposed to be covalent, sometimes to be co-ordinate and indicates localised pair bonds. According to the absorption spectra and photo-dissociation, the bond energies remain constant and additive so long as inorganic molecules possess  $p$ - $p$  bonds only, as in  $\text{SOCl}_2$  or  $\text{PCl}_3$ , but change entirely, when the central atom possesses its maximal number of valencies, as in  $\text{SO}_2\text{Cl}_2$  or  $\text{PCl}_5$ , indicating the splitting of the  $s^2$  group.<sup>9</sup>

(10) The vibrational analysis of the band spectra of  $\text{SeO}$  and  $\text{SeO}_2$  shows, that the energy of excitation, the symmetric valence vibration of both the unexcited and the excited term of  $\text{SeO}_2$  have practically the same value as the excitation energy and the vibrational frequencies of the corresponding terms of  $\text{SeO}$ . The same obtains from the analysis of the band spectrum of  $\text{SO}_2$ , whose corresponding constants closely resemble those of  $\text{SO}$ . This indicates strong localisation of the bonds and is corroborated by infra-red and Raman spectra, because

(11) The internuclear distances and vibrational frequencies of the constituent radicals remain very often unchanged in different polyatomic molecules.<sup>10</sup>

(12) Neither X-ray spectra nor physico-chemical measurements, like parachor, optical activity, etc. are qualified to establish different types of non-electrovalent linkages (semipolar double bond, singlet linkage) in non-aromatic molecules of the first order. Throughout the Periodic Table the maximal valency of all atoms is identical with the number of their outside electrons, and the next lower one in the main groups with that of their outside  $p$ -electrons alone. From these and other considerations it appears, as if the experimental facts of chemistry are best represented by a uniform pair bond theory of linkage as far as non-aromatic molecules of first order are concerned.<sup>11</sup>

<sup>7</sup> H. Lessheim and R. Samuel, [*Proc. Phys. Soc.*, (Lond.), 1934, 46, 523] when suggesting this explanation, had to use estimated values for the anomalous term of  $\text{C}$  and it is not impossible that these values are slightly too high. But even an error of 3 volts would represent only 10% of the 33 volts energy of adiabatic dissociation of  $\text{CO}_2$ , which follows from its infra-red spectrum and any other plausible explanation of this high value does not appear to be possible.

<sup>9</sup> R. K. Asundi and R. Samuel, *Proc. Phys. Soc.*, (Lond.), 1936, 48, 28. Mohd. Jan Khan and R. Samuel, *ibid.* (in press) and forthcoming papers of this laboratory.

<sup>10</sup> R. K. Asundi and R. Samuel, *Proc. Ind. Ac. Sci.*, (Bangalore), 1935, 2, 30; R. K. Asundi, Mohd. Jan Khan and R. Samuel, *Nature*, Oct. 19, 1935, 136.

<sup>11</sup> R. F. Hunter and R. Samuel, *J.C.S.*, 1934, 1180; *Rec. Tr. Chim.*, Pays-Bas, 1935, 54, 114; *Chem. and Ind.*, 1935, 54, 31, 467, 635.