257. *The Problem of Chemical Linkage. Part I. An Interpretation of Valency on the Basis of Wave-Mechanics and Band Spectra.*

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IT becomes increasingly evident that certain assumptions of current electronic theories of chemistry are physically unsound, and the object of these papers is to apply knowledge obtained from band spectroscopy and wave-mechanics to the problem of valency and molecular structure. This has led us, we believe, to a generalised theory in which many of the major difficulties have been overcome.

Fundamental Wave-mechanical Principles.—The problem of chemical linkage can be approached by means of wave-mechanics from two entirely different points of view. The original theory of London (*Z. Physik*, 1928, **46**, 455), which belongs to the " electron-pair bond theories," considered neutralisation of electronic spin of primary importance, but led to an unsatisfactory generalisation, since it dealt only with configurations of atoms possessing uncounterbalanced spin. Hund has shown (*ibid.*, 1932, **73**, 1; **74**, 429), however, that the essential feature of chemical combination consists in the entry of electrons, originating in different atoms, into the same group in the electronic configuration of the molecule, neutralisation of spin being more in the nature of the operation of Pauli's principle (cf. also Slater, *Physical Rev.*, 1931, **37**, 481; Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225). Recently, an alternative method of approach has been developed by Mulliken (*Chem. Reviews*, 1931, **9**, 347; *Physical Rev.*, 1932, **41**, 49) and Herzberg

(*Leipziger Vorträge,* 1931) which may be termed the "theory of molecular orbitals." * It must be clearly understood that both theories commence with *postulates,* since actual wave-mechanical calculations are only possible in cases of the simplest diatomic molecules. The former commences with the postulate that covalent linkage is always due to the formation of *pairs* of electrons originating in different atoms, whereas the theory of molecular orbitals assumes that single electrons are already capable of contributing to chemical linkage (in a positive or negative sense) irrespective of the atoms from which they originate. The pair theory therefore explains the saturation of valency, while the theory of molecular orbitals can only accomplish this by the introduction of further assumptions, which are in reality generalisations of pre-wave-mechanical theories, *e.g.*, the "octet rule."

The validity of the foundation postulate of the pair-bond theory rests on the fact that the bonding power of an electron pair has been established by actual wave-mechanical calculation in a number of cases (*e.g.*, hydrogen; Heitler and London, *Z. Physik*, 1927, **44**, 455). It can be shown, however, that a single electron does not possess bonding power, since the formation of the hydrogen molecule ion $[H_2]^+$, which is quoted as a proof of the theory of molecular orbitals (Mulliken, *loc. cit.*), depends essentially on the identity of the two positive hydrogen nuclei (Teller, *Z. Physik*, 1930, **61**, 458), and this case has therefore nothing to do with ordinary chemical linkage.

Some electronic groups of diatomic molecules possess a maximal number, not of two, but of four electrons, and chemical combination occurs in reality between an electron of one atom and the *whole electronic configuration* of the second. In polyatomic molecules, however, only groups with a maximal number of two electrons occur, and since we are primarily concerned with the development of a simple theory which is workable from the point of view of chemistry, chemical combination may be regarded as the entry of an electron of one atom along with an electron of the second into the same energetic group of the molecule. Lewis's original conception of two shared electrons per covalency is therefore correct in a certain sense, although recent investigations of the band spectra of diatomic molecules of the type of beryllium oxide indicate that there is no justification for many of the later developments of this theory. Thus the outer electrons of the atoms of Group II possess in their lowest energy level the configuration s^2, and it has been shown by London (*loc. cit.*) that this sub-group cannot form a chemical linkage until it has undergone fission and at least one electron has been transferred to the p-group. This has been generalised by Hund (*loc. cit.*) to show that neither between the groups $(s^2)(s^2)$ nor between the group (s^2) and a group (p^2) or (p^4) is chemical linkage possible. Moreover, Herzberg (*loc. cit.*) has shown experimentally that the ground level of beryllium oxide possesses a single covalency, formed between unexcited oxygen and beryllium in the next higher term in which it possesses one s and one p electron; the double bonded structure Be = O occurs only in an excited level of the molecule (Lessheim and Samuel, *Z. Physik*, 1933, **84**, 637). Particular interest attaches to these results since the s^2 group constitutes the "lone pair" of electrons to which the formation of co-ordinate covalencies is attributed in current theories. Attention may also be directed to the odd-electron molecule of nitric oxide, which in its ground level possesses the configuration

$$K_1K_2 2s\sigma^2(2s)3p\sigma^2(2s)2p\pi^4(2p)3d\sigma^2(2p)3d\pi(2p)$$

in which the $2p\pi^4$ and $3d\sigma^2$ groups contain two p-electrons of nitrogen and the four p-electrons of the oxygen atom (Lessheim and Samuel, *loc. cit.*). If one of these is excited, the molecule as a whole passes from its ground level $^2\pi$ (χ) to the excited $^2\pi$ (B) term; the dissociation energy being decreased thereby from 6·7 electronic volts (*ca.* 154,000 cals.) to 4·5 electronic volts (*ca.* 103,000 cals.), due to the rupture of one pair of sharing electrons. If, however, the single $3d\pi$ electron which constitutes the free valency of the molecule is

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* The theory of molecular orbitals as a theory of chemical linkage must, of course, be distinguished from the method of molecular orbitals used in calculating the terms and electronic configurations of a system of two or more atoms (Lennard-Jones). As a matter of principle, its results will include all attractive and repulsive terms of the system, and since it is not clear in which way intersections of terms occur, it cannot determine the energetic order of electronic levels without further assumptions.

excited, the dissociation energy increases to 10·7 electronic volts in the $^2\Sigma$ term, whose origin is the combination of an oxygen atom with an atom of nitrogen possessing the electronic configuration $2s^2 3p^2 3s$. This indicates that, so long as the odd electron is unshared, it tends to disturb the linkage in such a way that the latter increases in strength the further the electron is removed, the free valency belonging essentially to nitrogen.

It is therefore clear that in the formation of a molecule two effects have to be considered, the first of which consists in the entry of electrons originating in different atoms into the same group in the molecule. This is of fundamental importance since on it depends whether chemical linkage can occur, and how many linkages can be produced. Superimposed on this, there is a second effect, termed by Mulliken (*loc. cit.*) the " premotion " of electrons, which depends essentially on the fact that electronic groups may be bound in the molecule in an energetical order other than they possessed in the original atom. This may influence the energy of the bond as indicated by its heat of dissociation, but the effect is only of second order in importance, and is insufficient to cause chemical combination (Hund, *loc. cit.*).

The Octet Rule, Co-ordinate Covalency, the Semipolar Double Bond, and the Theory of the Singlet Linkage.—It is clear that the pair-bond theory recognises therefore only one form of non-electrovalent linkage, and if strictly followed does not lead to the octet rule. It is true that, if only negative valency is considered, oxygen for instance being regarded as possessing two gaps in its electronic configuration relative to neon, octet formulæ can be constructed for molecules such as N_2, O_2 and F_2. Obvious difficulties occur, however, with regard to positive covalency, as is indicated in the following table, in which the numbers of electrons in the outside shells around the central atoms are given below the formulæ for the molecules concerned.

$AgCl$.	$BeCl_2$.	BCl_3.	CF_4.	PF_5.	SF_6.	IF_7.
2	4	6	8	10	12	14
		$InCl$	CO	PCl_3	SO_2	IF_5
		2	4	6	8	10
					SO	ICl_3
					4	6
						ICl
						2

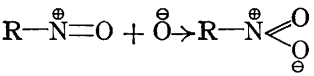
This was evidently the genesis of assumptions such as those of the semipolar double bond and the singlet linkage. It is instructive to note, however, that the first line of figures represents exactly double the total number of valency electrons ($s + p$) of the atoms concerned, and that those of the second line are double the number of p-electrons of these elements.

The theory of co-ordination, as postulated for the case of the nitro-group (Sidgwick, " The Electronic Theory of Valency," 1929, p. 65), involves the transfer of the lone pair of electrons of the nitrogen atom of the nitroso-group to a second oxygen atom, $-\mathrm{N}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\searrow\mathrm{O}}$. The lone pair constitutes, however, a closed helium-like group which cannot undergo chemical reaction until it is split, and nitrogen assumes the excited p^5 state. When this occurs, the five linkages originated by five identical p-electrons are equivalent, and the correct formula for the radical is therefore $-\mathrm{N}\ll\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$. This is in agreement with the equivalence of the two oxygen atoms (Ingold, J., 1933, 1120) established by the zero dipole moments of p-dinitrobenzene and 4 : 4'-dinitrodiphenyl (Williams, *Physikal. Z.*, 1928, **29**, 174, 683). The high dipole moment of the nitro-group should therefore be regarded as the vectorial sum of the two linkages between nitrogen and oxygen, and it is interesting to note that the infra-red spectrum of sulphur dioxide indicates a similar equivalence of the two oxygen atoms in this molecule (Bailey and Cassie, *Proc. Roy. Soc.*, 1933, *A*, **140**, 605).

With regard to the parachor of nitro-compounds, Sugden, Reed, and Wilkins (J., 1925, **127**, 1185) assume that nitrogen possesses a constant value of 12·5, and attribute the difference between the calculated and the empirical parachors of nitro-compounds to a difference in the mode of linkage of the second oxygen atom. There is clearly the alternative possibility, however, that nitrogen possesses different parachor values in the ter- and the quinque-valent state, and this interpretation of Sugden's observations has already been suggested by Sippel (*Ber.*, 1930, **63**, 2185), since the reverse distribution is conventionally assumed in molecular refractivity, which is very closely allied to the parachor.*

Whenever the s^2 group is split to obtain bonding power, the electrons form closed groups in the molecule, together with the electrons of the second partner. If, therefore, it is assumed that, in co-ordination, two electrons enter the molecule without sharing with electrons of the acceptor and remain a separate group in the electronic configuration of the product, no chemical union has occurred. If, on the other hand, it is assumed that they form a group or groups with the electrons of the acceptor, no distinction is possible between the linkages formed in this way and what Sidgwick terms " normal " covalencies.

Lowry's view that a semipolar double bond consists of a covalency and an electrovalency (J., 1923, **123**, 822, and later), symbolised as $-\overset{\oplus}{N}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow \underset{\ominus}{O}}$ for the nitro-group, is not excluded by wave-mechanical principles in the present state of knowledge. On the basis of this, the formation of the nitro-group is evidently to be interpreted as the fission of the s^2 group of the nitrogen atom of the nitroso-group with the transference of an electron to the oxidising oxygen atom, followed by the combination of this ion O^- with the nitroso-cation by means of an additional covalency :



$$R-\overset{\oplus}{N}=O+\overset{\ominus}{O}\rightarrow R-\overset{\oplus}{N}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow \underset{\ominus}{O}}$$

This interpretation of co-ordination excludes, however, all cases of combination in which the acceptor does not possess a high electronic affinity ; *i.e.*, all cases in which the acceptor does not possess at least half the *p*-electrons of the next inert gas, and all those in which the electro-affinity is already saturated. The only cases which need be considered are, therefore, those compounds which in pre-electronic formulation received double bonds connecting atoms possessing considerable electronic affinity (*e.g.*, nitrogen peroxide, sulphur trioxide, etc.). It can be shown, however, that such linkages will not occur for energetical reasons, since the ordinary covalent structures represent a much lower energy level, due to the very high energy of ionisation of *s*-electrons (*e.g.*, 25·3 electronic volts for nitrogen).

It is clear that remarks similar to those made with regard to co-ordinate covalency are applicable to the theory of singlet linkages (Prideaux, *Chem. and Ind.*, 1923, **42**, 672 ; Sugden, J., 1927, 1176, and later). Either the electron of the singlet forms a group together with one or more electrons of the second atom, in which case it is an ordinary covalency, or it is alone in a separate group and cannot therefore constitute a genuine chemical linkage. The suggestion made by one of us (Hunter, J., 1930, 125), that the labile bromine atoms in compounds of the type of benzthiazole dibromide are linked to the ring nitrogen atom by means of single electronic linkages, is therefore withdrawn.

Attention may now be directed to certain cases in which the octet theory appears to be formally correct, but leads actually to results which are inadmissible in the light of spectroscopic evidence. The simplest of these is probably furnished by the oxygen molecule, which is usually written $:\overset{\bullet\bullet}{O}\overset{\times}{\underset{\times}{\cdot}}\overset{\times\times}{O}\overset{\times}{\underset{\times}{}}$. Actually, however, the " octet " is not a closed and stable configuration, since the lowest energetic level of the molecule is a $^3\Sigma$ and not a $^1\Sigma$ term, indicating that there are two π electrons whose spin is uncounterbalanced in an unclosed group, which would be *p*-electrons in the separate atoms. The molecule therefore possesses paramagnetic properties and should be written $=O=O$, and in this connexion it is interesting to note that hydrogen peroxide has now been isolated in a second form

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* The optical activity of the toluenesulphinic esters discovered by Phillips (J., 1925, **127**, 2552) is no proof of the existence of the alleged semipolar double bond in such compounds. The necessary condition for optical activity is that sulphur should occupy the apex of the tetrahedron, and that it should possess strong positive polarity.

which appears to possess the structure $\begin{matrix}H\\H\end{matrix}\!\!>\!O{=}O$ (Geib and Harteck, *Ber.*, 1932, **65**, *B*, 1551). Similarly, molecules such as those of the halogens are known to exhibit definite dipole moments although the atoms concerned should clearly be equivalent on the basis of octet formulæ of the type $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:$.

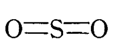
Another very serious difficulty in connexion with conventional electronic theories of valency is the facile transition from covalency to electrovalency. For instance, the band spectrum of silver chloride indicates that it is covalent in the gaseous state (Franck and Kuhn, *Z. Physik*, 1927, **43**, 164, and later), but in the fused state and in solution it is obviously electrovalent. Similarly, hydrogen chloride is covalent in the gaseous and the liquid state and heteropolar in aqueous solution.

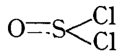
Sidgwick (*op. cit.*, p. 72) has explained the existence of the polymerised form of hydrogen fluoride and the double salt KF,HF by an expansion of the valency group of hydrogen to four, which Sugden ("The Parachor and Valency," 1930, p. 149) has criticised as a violation of Pauli's principle. The later contention of Sidgwick and Bayliss (J., 1930, 2027), that a second quantum group is permissible on Pauli's principle, is, however, meaningless, since wave-mechanical calculations prove that it is impossible for electrons to enter the 2*s* group while the 1*s* group already possesses its maximum number of electrons, and the curve of the potential energy of the third electron has no minimum and exhibits only repulsion from the system. If the filling up of the higher groups did not depend also on nuclear charge, then clearly ions such as $[He]^-$ and $[He]^{--}$ should be capable of existence. In our view, the polymerisation of hydrogen fluoride and the existence of Frémy's double salt are merely the result of enhanced dipole association whose occurrence is mainly observed in the first period on account of the small dimensions of these elements.

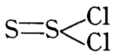
Similar remarks apply also to the alleged $[F\rightarrow BF_3]^-$ ion (Sidgwick, *op. cit.*, p. 68), since $[BCl_4]^-$ ions do not exist. There appears to be nothing in the properties of the fluoroborates themselves which calls for special explanation, since the recrystallisation of these salts is known to give rise to mixtures containing alkali fluorides and metaborates (Mellor, "A Comprehensive Treatise, etc.," Vol. VI, 944). Furthermore, Ulich and his collaborators have shown (*Z. angew. Chem.*, 1931, **44**, 750; *Z. physikal. Chem.*, 1932, *B*, **16**, 153, and later) that the complexes formed by the boron and the aluminium trihalides and the dihalides of beryllium with amines and alcohols are mere loose dipole associations, and that there is therefore no evidence of "octet completion" of the type, $Cl_3Al\rightarrow NH_3$, pictured by Sidgwick (*loc. cit.*). The chemical individuality of the supposed silicofluorides appears to be of a similar doubtful character (Mellor, *op. cit.*, Vol. V, 124), and in our opinion there is no comparison between the existence of the alleged co-ordinated $[SiF_6]^{--}$ ion and that of sulphur hexafluoride (Sidgwick, *op. cit.*, p. 68), since the stability of the latter arises from the fact that sulphur possesses six valency electrons, and not from the presence of a hypothetical dodecet group of electrons.

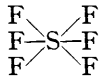
The Theory of a Single Form of Non-electrovalent Linkage.—It is our view, therefore, that there is only *one form of chemical linkage, viz.*, covalency, whose polarisation may vary anywhere between the limits of zero in the hydrogen molecule and that of a true salt consisting of ions held together by electrostatic attraction; further, that chemical union consists always in the coupling of atoms by means of entry into the same group in the molecule of two electrons possessing anti-parallel spin. An atom which possesses at least half the *p*-electrons of the configuration of the next inert gas in the periodic system can take up additional electrons to obtain its closed shell, but in doing this it acquires a certain degree of negative character, and the atom the electron of which is bound by the whole electronic configuration of this negative partner acquires a corresponding degree of positive polarity. In any molecule, therefore, at least one atom must be regarded as the *centre* of positive polarity. In electrovalency such as occurs in Na^+Cl^-, the positive partner has completely relinquished its electron, which has been taken up by the *p*-electrons of the chlorine atom, the spin of the last of which it cancels with the formation of the $[Cl]^-$ ion. In the covalent linkage between silver and chlorine in the vapour of silver chloride, however, the electron of the silver has shared the configuration of the chlorine nucleus but is still partly governed by the electrical field of the silver atom. The metallic atom has not yet attained the krypton configuration, nor has chlorine wholly acquired the argon structure, but both are striving towards these ends, and the additional energy provided by fusion is sufficient to carry the process to completion. If this is taken as a typical case of covalency it follows that : (i) any atom may act as a positive partner in chemical combination, a fact which is not obvious on the basis of current theory ; (ii) the maximal number of " positive " valencies of an atom is equal to the number of electrons in its outer shell; (iii) the transition from covalency to electrovalency depends merely on the energy with which the electrons of the positive partner are held to its nucleus and the electronic affinity of the negative partner.

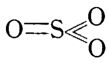
On the foregoing basis, the obvious difficulties with regard to valency numbers disappear. In the place of the octet rule, which is only successful in explaining the behaviour of Group IV and bivalency in Group VI, the fundamental basis of our theory becomes *a closed group or sub-group residue,* which may or may not be a group of eight electrons. Sulphur, which possesses six valency (two *s* and four *p*) electrons, therefore exhibits quadricovalency when only the latter are active as in sulphur dioxide, thionyl chloride, and sulphur monochloride (Lorenz and Samuel, *Z. physikal. Chem.*, 1929, *B*, **14**, 219), and hexacovalency as in sulphur hexafluoride and sulphur trioxide when the s^2 group is split and these electrons are also raised to the *p*-state :











In this connexion it will be observed that all the electrons of the sub-group become active together, explaining thereby the phenomenon of saturation of valency. By sharing with the electronic configuration of the negative partner, it will be seen that these electrons automatically become electrons of a closed group ($^1\Sigma$ term of the molecule), and this justifies us in considering only the residual outer electrons of the positive partner as regards stability of configuration. In quadrivalent sulphur, in its dioxide for instance, both oxygen atoms have completed their *L* shell and sulphur remains with its unshared electrons in the helium-like s^2 group. In the hexafluoride, however, sulphur is left with the *K* and *L* shells of the neon structure, all the outer electrons taking part in closed groups created by sharing with fluorine.

That we are justified in regarding not only the closed shell but also the *closed group* as stable, follows from spectroscopical evidence. For instance, the spectroscopical indication of a stable group is a $^1\Sigma$ term, which, like the $^1S_0$ term of the inert gases, shows that all electronic vectors are counterbalanced. The $^1\Sigma$ term is a property not only of molecules such as those of hydrogen fluoride, chlorine, and nitrogen, which possess octets, but also of the elements of Group II in which there are two *s*-electrons outside the closed shell. This enables us to carry over the simpler terminology of the electronic configurations of atoms (*s* or *p* electrons) to molecular structures (σ or π) for the purpose of obtaining a working model which is still a reasonable approximation to atomic physics, but capable of application to complex chemical structures.

The full import of these deductions will be seen by reference to the table on p. 1182. Iodine with the configuration $s^2 p^5$ may possess any odd covalency between 1 in the monochloride and 7 in the heptafluoride, and aluminium exhibits stable tervalency in its chloride despite the fact that the octet of the central atom is incomplete. The difference between nitrogen and phosphorus with regard to ease of conversion from the ter- into the quinque-valent state arises, not from a difference of mechanism, but from the difference of energy with which the valency electrons are held to the nucleus (*e.g.*, $N = N^{5\oplus} + 5e + 270$ volts; $P = P^{5\oplus} + 5e + 170$ volts); quinquevalency being dependent, not only on the *p*-electrons, but also on the *s*-electrons which are held with an energy considerably greater than the former (*e.g.*, $P = P^{3\oplus} + 3e + 61$ volts). Similarly, the elements of Group IV, which contain two *p*-electrons and two *s*-electrons in their outer group, are capable of exhibiting bivalency and quadrivalency, in which connexion attention may be directed to the structure of carbon monoxide.

It is by no means clear which electrons are supposed to be responsible for the alleged co-ordination $\mathrm{C} \overset{\leftarrow}{\equiv} \mathrm{O}$ (Hammick, New, Sidgwick, and Sutton, J., 1930, 1876). The known physical facts regarding this molecule are as follows. The ground level, like that of CSi and SiO, is a $^1\Sigma$ term, and six *p*-electrons, only two of which originate from carbon, form a $\pi^4(2p)$ and a $\sigma^2(2p)$ group. Carbon monoxide is therefore saturated, and possesses the classical formula $\mathrm{C{=}O}$, and one of its $\sigma^2(2s)$ groups must undergo fission with the production of an excited carbon atom before it can give rise to the dioxide or to carbonyl chloride. The carbonyl group cannot therefore possess the same configuration as carbon monoxide, and the comparison of dipole moments of bi- and quadri-valent compounds of carbon (Hammick, New, Sidgwick, and Sutton, *loc. cit.*) cannot be accepted as any proof of the existence of a third linkage in the molecule. The high frequency of the Raman effect, or, in other words, the high dissociation energy of the molecule, does not appear so exceptional as to require special explanation. Thus the energy of dissociation for a single covalency, as deduced from band spectra in the first period, is 4·9 electronic volts for the link H–O, 5·8 for Be–O, 6·6 for B–O, and the double link in nitric oxide has a value of 6·7 as long as it is disturbed by the proximity of the odd electron, which rises to 10·7 as soon as this is removed to the next group. The value of 10 volts for the double bond in carbon monoxide is therefore perfectly reasonable. It may also be noted that Pauling's deductions with regard to the structure of this molecule (*J. Amer. Chem. Soc.*, 1932, **54**, 988) are incorrect both on the basis of his assumed value of 3 volts per covalency, and on the electronic configuration of the terms and their dissociation (Lessheim and Samuel, *Curr. Sci.*, 1934, 2, 347).

This paper has been confined to what, for the lack of a better expression, may be termed valency of the first order. The problem of the transition elements and the nature of Werner's true complex salts and chelated compounds will be dealt with in a future communication.

We wish to express our best thanks to Dr. Lessheim, of this University, for much helpful criticism with regard to the wave-mechanical aspects of this paper.

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