ELECTRONIC CONFIGURATION AND BOND ENERGY.

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Introduction.

Among the many band spectra of diatomic molecules known at the present time, if one excludes the permanent gases, those of the oxides have been easily the earliest to be observed. Lately, however, the number of band spectra of fluorides, chlorides, sulphides and of a few oxides which were still unobserved have been recorded and analysed by various authors. Even now the number of molecules whose spectra one would like to know is not large but a beginning can be made by a systematic survey and comparison of available data, to understand empirically the relationship between the bond energies determined by the spectra and the place of the constituent atoms in the periodic system on the one hand and the electronic configuration of the completed molecule on the other. In this paper we propose to start such an attempt. We shall not treat the hybrides because they approach closely the united atom and are a class by themselves. The oxides and halides of the second group and the oxides of the fifth group have been dealt with recently from a similar point of view[1] and these results will be bodily taken over for our present purpose.

Electronic Configuration and Dissociation Products.

(a) *Oxides of the third group.*—Since the halides of the alkali metals are electrovalent and the diatomic molecules formed by atoms of the second group are already dealt with, we start with the oxides of the third group. In addition to BO and AlO which have been known for some time we now know also GaO. Particular interest attaches itself to this because there exist two different theories on the connection between dissociation energy and electronic configuration, with which we shall deal presently below. The spectrum of BO has been discussed by Mulliken[2] from the view-point of his theory and that of AlO which is quite different from BO as far as dissociation energy is concerned, is discussed by Lessheim and Samuel[3] from the view-point of their theory. The spectrum of GaO is therefore

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likely to bring about a decision on this question as far as the oxides of the third group are concerned.

In gallium oxide one band system[4] involving two $^2\Sigma$ terms is known for which the energy of excitation is 3.17 volts and the dissociation energies are 2.82 v. for the ground level X $^2\Sigma$ and 4.58 v. for the excited level B $^2\Sigma$. The energy difference of the products of dissociation is 4.93 v. (Fig. 1).
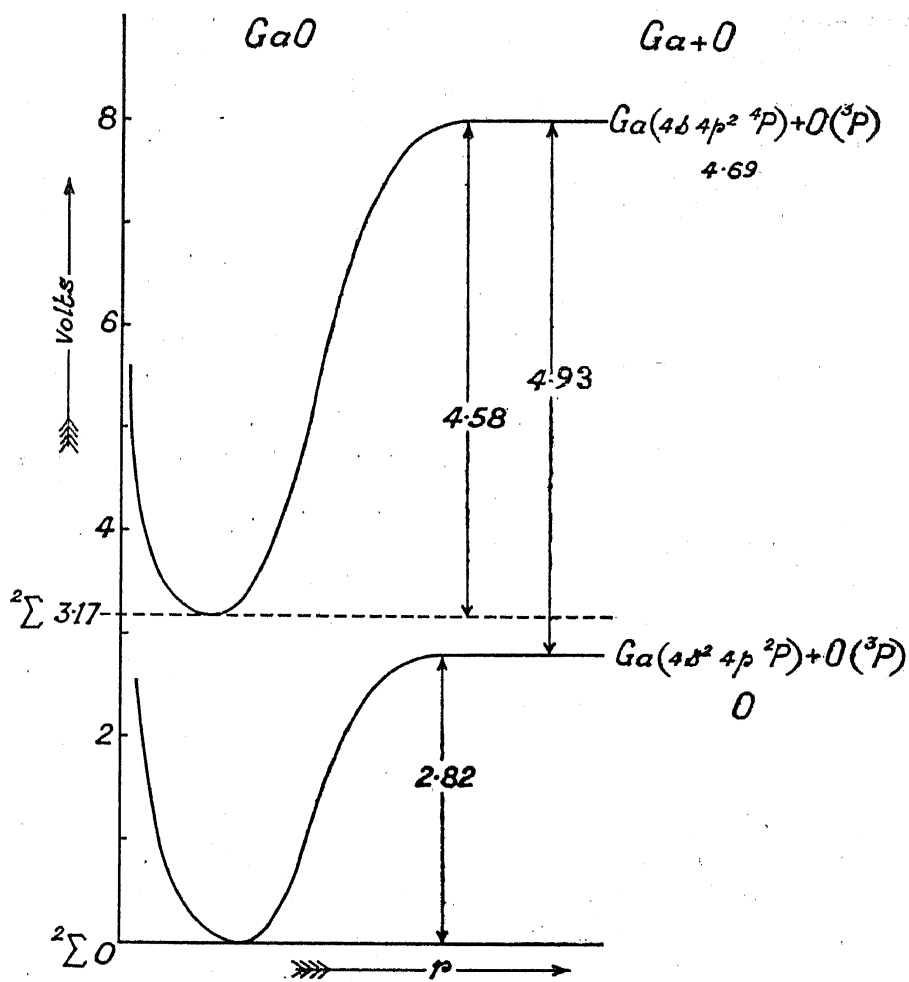

FIG. 1.

Exactly as in AlO, this constitutes a typical example of a molecule for which the dissociation energy increases on excitation.

The interpretation of such states of molecules really involves the essential difference between the two methods of treatment mentioned above. The method of molecular orbitals yields, as is well known, all the electronic configurations which give rise to the totality of electronic terms of a molecule. It is, however, not competent to distinguish the stable or attractive terms from the unstable or repulsive ones except by the introduction of

an additional hypothesis. One such hypothesis (Herzberg, Mulliken) is that the dissociation energy of a molecule is the resultant of the contributions of the single bonding and anti-bonding electrons; these are recognised as the non-premoted and premoted electron and the change of dissociation energy in the various states is attributed to the process of premotion. In the other view only those electrons contribute to the dissociation energy of a given level which, coming from different atoms, join to form pairs on the same molecular orbital. The essential difference between the two view-points therefore is that while for the first one the premotion has the first order effect and interaction between the electrons (other than that represented by a screening effect) only a subsidiary influence, exactly the reverse is true for the second method. On the basis of the latter view an increase in the dissociation energy of a molecule on excitation may then be due either to the removal of the odd electron, which represents a free valency as in BeF or NO, or to an increase in the number of electron pairs, giving rise to an increase in the number of chemical bonds, as for instance in BeO. The oxides of the third group are further examples of the latter case. Therefore in GaO as in AlO according to this interpretation we would expect that the term with an increased energy of dissociation is formed by the combination of unexcited oxygen with the Ga atom possessing two p-electrons, the s^2 group having undergone previous fissure. This is indeed borne out by experiment. The difference in the energy of the dissociation products is 4.93 volts and represents the energy of the transition $(4s^2\ 4p\ {}^2P) - (4s\ 4p^2\ {}^4P) = 4.69$ volts, which is indeed the lowest one of all those, which possess two p-electrons. There is, however, a term in which the s^2 group is intact, i.e. $(4s^2\ s\ {}^2S)$ in Ga with an excitation energy of 4.64 volts. If this term is correlated to the upper level of the band system why other similar but lower terms like $(4s^2\ 5s\ {}^2S)$ or $(4s^2\ 4d\ {}^2D)$ are passed over in the process of formation of the GaO molecule, will be completely ununderstood. On the other hand, it is particularly significant that the strongest system of the GaO bands directly gives an empirical and straightforward correlation to the configuration of Ga with two p-electrons. From the configuration Ga $(4s^2\ 4p\ {}^2P) + O$ $(2s^2\ 2p^4\ {}^3P)$ many configurations for the molecule GaO are possible of which the following will have the lowest energy :—

$$s\sigma^2\ (s),\quad p\sigma^{*2}\ (s),\quad p\pi^4\ (p),\quad s\sigma\ (p)\qquad {}^2\Sigma$$

According to the above correlation the excited level is obtained by a combination of Ga, $(4s\ 4p^2\ {}^4P)$ with O, $({}^3P)$. The energetically lowest possible configuration of this combination is :—

$$s\sigma^2\ (s),\quad p\sigma^*\ (s),\quad p\pi^4\ (p),\quad s\sigma^2\ (p),$$

the resulting term is indeed a $^2\Sigma$ in agreement with the experimental result. The increased energy of dissociation in the excited state is due to the formation of an additional bond. In the ground level, according to the conceptions of the pair-bond theory of linkage, (see below), only one bond is formed because, the s-electrons of Ga remain as a group by themselves in the GaO molecule and therefore do not take part in the linkage, and only the single p-electron joins with the electrons of O in a common molecular orbital. From a comparison of the two electronic configurations, it will be seen that the odd $s\sigma$ (p) electron belongs essentially to the O atom and that the single bond is formed in the $p\pi^4$ (p) group which is made up of three p-electrons of O and one of Ga. In the excited state this group remains intact. But the second p-electron of Ga, which is now available after the splitting of the s^2 group, joins the odd p-electron of O, completing the $s\sigma$ (p) group and thus giving rise to an additional bond.

These results are in complete harmony with those of AlO, where also the increase in dissociation energy in the excited state is brought about by an additional $p-p$ bond formed in exactly the same way. Thus among the three oxides of the third group whose spectra are known, two confirm the predictions of the pair-bond theory. The known spectra of BO alone indicate a different behaviour. The extrapolated dissociation energies correlate the lowest term of the BO molecule with excited terms of the separated atoms, and the excited terms of the normal atoms with the excited molecular state. Mulliken assumes that the extrapolated value for the lowest term of the molecule is too big and so makes it join the level of the unexcited atoms. If this is true, the term with an increased energy of dissociation, corresponding to that in GaO and AlO is not yet observed. Thus though BO does not support our explanation, it also does not contradict it. We are, however, inclined to believe that the X $^2\Sigma$ term of BO does not correspond to the ground level of GaO or AlO but to the excited level with increased energy of dissociation. From our experience about the extrapolated dissociation energy in a large number of similar molecules, we rather think that the reduction of 30% which is necessary for a correlation term of unexcited atoms is too much. The dissociation energy of this particular excited $^2\Sigma$ level has been found to be 4.6 volts in GaO and 6.2 volts in AlO, and therefore the extrapolated energy of 9.3 volts of X $^2\Sigma$, in BO, is about the correct order of magnitude.

(b) *Halides of the fourth group.*—Molecules possessing free valencies in the ground state are next met with among the halides of the fourth group. On account of the two p-electrons of the atoms of this group oxides and sulphides are stable molecules ; the diatomic halides, however, are, from the

standpoint of chemistry, only radicals. Like molecules of the type CaF or NO, these halides of the fourth group should therefore possess excited electronic terms which are more stable than their ground levels if the electron representing the free valency is partly removed by excitation to a higher group. Among the spectra of such molecules, indeed three cases are known in which this statement has been already confirmed. These are the molecules SiF, SiCl and SnCl. Among other molecules which have been mostly observed in absorption, the corresponding term with increased energy of dissociation has not yet been found. The molecule SnCl has been already discussed earlier[3,5] and it is shown that the combination of unexcited atoms in their configurations Sn ($5s^2\ 5p^2\ ^3$P) *plus* Cl (^{2}P) gives rise to a number of terms among which the ground state $^2\Pi$ with an energy of dissociation from 3.2 to 3.5 volts is one. The electronic configuration of the molecule in this state is :—

$$\sigma^2(s),\quad \sigma^{*2}(s),\quad \pi^4(p),\quad \sigma^2(p),\quad \pi^*(p)\qquad ^2\Pi.$$
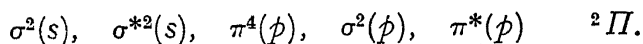
By an excitation of 4.2 volts we get to a $^2\Sigma$ state of the molecule for which the energy of dissociation is 4.8 volts and which is formed by the combination of unexcited Cl and excited Sn in the configuration ($5s^2\ 5p\ 5d$). The electronic configuration therefore is :—

$$\sigma^2(s),\quad \sigma^{*2}(s)\ \ \pi^4(p),\quad \sigma^2\ (p),\ldots\ldots,\ \sigma(d)\qquad ^2\Sigma.$$
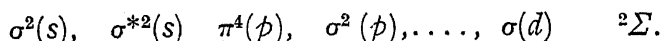
From a comparison of the two atomic and the two molecular states it is evident that the predictions of the electron pair-bond theory are confirmed.

These conclusions are fully corroborated by two more molecules whose spectra have been recently analysed. The ground level of the molecule SiF ($^2\Pi$), has the following configuration[6] similar to that of SnCl :—

$$\sigma^2(s),\quad \sigma^{*2}(s),\quad \pi^4(p),\quad \sigma^2(p)\quad \pi^*(p),\qquad X\ ^2\Pi.$$
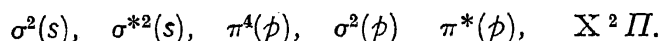
It is formed by the combination of unexcited atoms Si ($3s^2\ 3p^2\ ^3$P) $+$ F (^{2}P), and has an energy of dissociation of 4.77 volts. Among the excited levels there exists a term B $^2\Sigma$ lying 4.29 volts above the ground level, having an increased energy of dissociation of 6.51 volts and the excitation energy of the products of dissociation (6.03 volts) correlates it to the level Si ($3s^2\ 3p\ 4p\ ^1$S) $+$ F (^{2}P). Its electronic configuration is :—

$$\cdots\cdots\ \pi^4(p),\quad \sigma^2(p),\quad \cdots\cdots,\sigma(p)\qquad B\ ^2\Sigma.$$
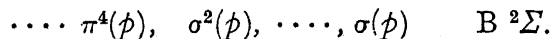
It will be seen that the configuration of the molecule in which the electron which does not contribute to the linkage is removed to a higher group, possesses an increased stability. Another excited term C $^2\Sigma$ for which the data are not very certain offers some evidence for a similar increase in stability if the non-binding electron of the Si atom is removed not to $4p$ as in the former case but to $4s$.

The data on SiCl are rather meagre and the constants are derived from but a few observations.[7] Only one band system is known which apparently belongs to the transition $^2\Sigma \to ^2\Pi$, the latter being the ground state of the molecule. The extrapolated value 4.98 volts for the ground level is much higher than what one would expect from analogy with SiF which has 4.77 volts for its dissociation energy in the ground state. Similarly there is little doubt that the extrapolated value of 11.59 volts for the energy of dissociation of the $^2\Sigma$ level is abnormally too high leading to an excitation energy of 10.81 volts of the dissociation products, which is too low for the first excited term of F and above the ionisation potential of Si. It is however certain that the excited $^2\Sigma$ level has an increased energy of dissociation and dissociates into normal F and a highly excited Si atom in which one of the p-electrons must have been removed to higher orbits.

Dissociation Energy and Electronic Configuration.

The relation between the energy of dissociation and the electronic configuration of the molecule can be further followed throughout the periodic system. We shall compare firstly the bond energy in a class of compounds along one particular period such as, *e.g.*, the oxides of Mg, Al, Si, P, and S. This will enable us to trace the effect of the electronic configuration on the energy of the bond. Secondly, we shall follow the course of the dissociation energy along the different periods, comparing molecules such as the oxides of the fourth group, *e.g.*, CO, SiO, GeO, SnO, and PhO. This will give us the influence of the varying field strength and polarity on the energy of formation of the molecule.

In Table I we have collected the energies of dissociation in the ground state of a number of molecules. They are obtained mostly by linear extrapolation, except those of O_2 and S_2 which are obtained from the convergence limit of the absorption bands. These values do not all possess the same accuracy, the extrapolation being based in some cases on but a few vibrational levels, which are themselves obtained from only a few observations. In some cases the spectra have not been sufficiently investigated to give us the exact nature of the term and some of the data are from absorption bands alone. Especially the values in brackets appear to be much less reliable than the rest.

In the case of S_2 and CO things are not yet definite. Interpretations of rotational pre-dissociations observed in these molecules have been used to evaluate their energy of dissociation in the ground state.[8] But these interpretations have to face some objections. Rotational pre-dissociation will certainly give rather accurate values of the heat of dissociation but it

TABLE I.*

	Be	Mg	Ca	Sr	Ba
F	5·4	3·7	3·2	3·1	
Cl	4·3	3·9	3·5		
O	5·8	3·8	3·88	3·28	
	B	Al	Ga	In	Tl
F					
Cl	3·6	3·6	(2·0)	(3·1)	(2·3)
O	(~6)	4·2	2·8		
	C	Si	Ge	Sn	Pb
F		4·8			3·4
Cl		(5·0)		3·8	3·2
O	~10	7·8	7·3	5·8	4·3
	N	P	As	Sb	Bi
F				~4	3·6
Cl					3·0
O	6·7	6·5	5·0	5·3	
	O	S	Se	Te	
O	5·09	~5·1	4·2		

* For this and the following tables the constants of the molecules are taken from W. Jevons: "Report on Band Spectra" (London, 1932) and H.Sponer: "Molekuel Spektren (Berlin, 1936). For PbF G. D. Rochester: *Proc. R. Soc.*, 1936, **153**, 407; BiF, BiCl, etc. F. Morgan: *Phys. Rev.*, 1936, **49**, 41. For SiF R. K. Asundi and R. Samuel (Ref. 6); SbF from unpublished data.

has to be established unmistakably as for instance in the case of MgH. Otherwise it will be difficult to distinguish between true rotational pre-dissociation for which a correlation to atomic levels is possible and the simple termination of band structure arising from rotational instability or from experimental conditions of excitation. In CO, for instance, the suggested interpretation is not compatible with Kronig's selection rule for multiplicity and the value of 8.41 volts for D (CO) leads to 107.9 K.cal./mol. for the heat of sublimation of carbon, a value which hardly can be reconciled with thermochemical data and particularly the behaviour of free radicals. In S_2 we have means of checking the interpretation of the abrupt termination of the rotational structure as genuine pre-dissociation. As we know,

the point of convergence in an absorption band spectrum is also one of the most accurate methods of deriving the energy of dissociation. Such a convergence limit for S_2 is found at $4.9 + 0.2$ volts.[9] If the dissociation products are normal atoms, this value is itself equal to D (S_2) ; or if we deduct once or twice the triplet separation of S (^3P), we obtain 0.07 or 0.14 volts less. On the other hand, if the products of dissociation involve a sulphur atom in the ^1D term, we obtain 3.8 ± 0.2 volts for D (S_2). None of these possible values agrees with 4.41 volts which is deduced from the interpretation of disappearance of rotational structure as true pre-dissociation. The wide discrepancy between the values on this interpretation and the data on convergence limit shows that the interpretations of pre-dissociation data are not always easy. For our present purpose therefore we take the values of $\sim$ 10 volts of D (CO) and 3.8 volts for D (S_2).

In spite of these difficulties certain characteristic changes do exhibit themselves quite clearly and we proceed to point out and discuss them. If we compare the diatomic *halides*, we find that the dissociation energy
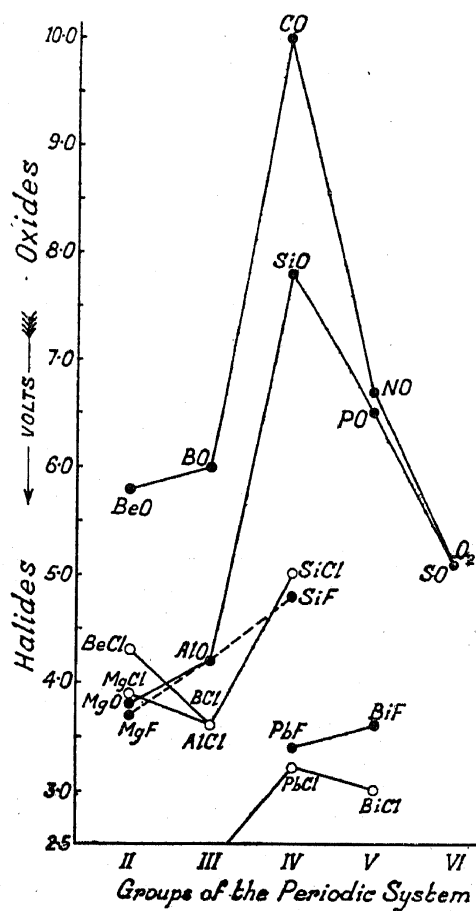

FIG. 2.

remains rather constant in the same period as will be seen also from the examples displayed in the diagram. There are slight differences, which indicate only a secondary superimposed effect. On the other hand, the energy appears to decrease from the second to the third group, but seems to rise again in the fourth group with a tendency to be rather constant later on. For example, BeCl has 4.3, BCl 3.6 volts showing the decrease from the second to the third group. AlCl with 3.6 and SiCl with something less than 5 volts indicate the increase from the third to the fourth group and so also do TlCl with 2.3 and PbCl with 3.2 volts. BiCl with 3.0 indicates a tendency for the dissociation energy to remain constant from the fourth to the fifth group.

We shall consider these tendencies from the view-point of the method of molecular orbitals. Firstly let us assume according to the original interpretation of this method, that each single electron contributes independently to the stability of the molecule as a bonding electron if it is not premoted, as an anti-bonding one, if it is premoted. From this standpoint, the ground levels of all the halides involve unexcited atoms. The outside s-electrons of the metal and the halogen form an unpremoted and a premoted σ^2 group, whose contributions to the bond cancel out and the linkage is produced by the p-electrons of the halogen atom alone in the earth alkali halides, and of the metal and the halogen both in the subsequent groups. Accordingly we get 5 unpremoted electrons in compounds like BeCl and 6 such electrons in BCl. The additional electrons in molecules of the subsequent types come now into non-premoted groups and SiF processes 6 bonding and 1 anti-bonding electron ($\pi^4\,\sigma^2\,\pi^*$), BiF 6 bonding and 2 anti-bonding electrons ($\pi^4\,\sigma^2\,\pi^{*2}$). Each electron represents half a positive or negative bond, as a consequence of which BeCl has $2\frac{1}{2}$, BCl 3, SiF $2\frac{1}{2}$ and BiF 2 bonds. This should show itself in an increase of the bond energy from BeCl to BCl, and a decrease from AlCl to SiCl, while just the reverse happens in each case. Here we have assumed, that all the p-electrons are on molecular orbitals. If it is presumed, that four of the p-electrons of the halogen remain on atomic orbitals, the disagreement is even more pronounced, because the percentage changes become bigger.

The other standpoint does not meet with any such difficulties. Here we obtain only a single bond in every case, because only such electron pairs contribute to the stability of the molecule in which electrons of both the atoms join, and because 4 of the p-electrons of the halogen atom form a π^4 group by themselves, only one electron joins in the same orbital with electrons of the metal atoms. The halides of the second group are formed according to this view by excited metal atoms with one s- and one p-electron,

for which experimental evidence seems to be convincing.[1] In BCl, SiF and BiF the metal atom possesses already a p-electron and is therefore capable of chemical union in its unexcited state. Thus we obtain everywhere the same type of a single p—p bond on which is superimposed the varying influence of the remaining electrons. An odd electron not contributing to the linkage may disturb and weaken it, but on the other hand, a hybridisation, *e.g.*, of the s and p functions as for instance in BeCl, may slightly strengthen the bond. Subject to such considerations this view-point certainly explains the course of the dissociation energy satisfactorily.

The superiority of this view-point becomes more evident from the following discussion of the *oxides*. In an oxide of the second group, according to the original interpretation of the method of molecular orbitals, again the two $\sigma^2(s)$ groups cancel out and the linkage rests on the four p-electron of oxygen alone, which are bonding electrons in the molecule. The ground state of the molecule being $^1\Sigma$ and that of O being ^{3}P, this interpretation has to assume, that it involves an oxygen atom already excited to ^{1}D. But also the combination of an unexcited metal atom of the second group with unexcited oxygen gives a bonding configuration with the same 4 unpromoted p-electrons of O and the resulting triplet term of the molecule should form either the ground level or at least a very low term in the electronic states of the molecules. But such a term has never been found. In any case oxygen having one electron less than a halogen, we obtain electronic configurations with one electron less than in the halides and accordingly 2 bonds in BeO, $2\frac{1}{2}$ in AlO, 3 in CO, $2\frac{1}{2}$ in NO, and 2 in O_2.

From the other view-point the known ground level $^1\Sigma$ of the earth alkali oxides is formed by neutral oxygen and a metal atom in the term sp ^{3}P. This has been corroborated by the correlation of the dissociation products of the higher electronic states of these molecules to atomic terms and particularly the occurrence of the anomalous terms of the metals leaves little doubt as to the justification of this correlation.[1] The molecules of the type of BeO possess therefore only a single bond in their ground state which has to be considered as a p—p or a hybridised sp—p bond. The oxides of atoms of the third group also possess only a single bond in their ground level, because only one p-electron is present in such unexcited metal atoms. The atoms of the fourth group are the first to possess two p-electrons in their unexcited state and therefore their oxides possess a double bond. The same holds for the atoms of the fifth and sixth groups, but their oxides possess one and two odd electrons respectively, which disturb and weaken the bond in the ground state.

Experimentally we find that the energy of dissociation remains constant or rather decreases from MgO and CaO to AlO and GaO.* From the discussion about BO, above, it is clear that the dissociation energy of unexcited BO is about 6 volts, whether the observed $^2\Sigma$ level is the ground level or not. This value is again identical with that of BeO and considerably less than that of CO. If we compare the oxides of the atoms of the fourth group with the corresponding oxides of the second and third group, we get the interesting result, that the energy of dissociation shows a big increase and is about doubled. In the next groups, molecules of the NO and SO types, the dissociation energy is again decreased in two distinct steps.

The decrease of energy as we go from the fourth group to the sixth finds its explanation equally well from both the above view-points, from the assumption of premotion in the one case, and from that of the disturbing effect of the odd electrons in the other. On the other hand, the observed change from the second group to the third and fourth groups, can only be explained by the second view-point. From the first view-point a regular increase would be expected, so that the oxide of the atoms of the third group would have a dissociation energy midway between the oxides of those of the second and fourth. But, as the discussion in the first section of this paper has shown, BO, AlO, and GaO possess about the same dissociation energy as the corresponding oxides BeO, MgO and CaO, and one half to two thirds of that of CO, SiO, and GeO. From the second view-point such a course of the dissociation energy is just what one would expect. So long as a single bond persists as it does in the oxides of the second and the third groups, the dissociation energy is roughly of the same order of magnitude; as soon, however, as we reach the fourth group where the pure double bond manifests itself without the presence of disturbing electrons, the dissociation energy suddenly increases to nearly double the value. This to our mind indicates another evidence in favour of an interpretation of the method of molecular orbitals as an electron pair-bond theory of valency.

We shall now follow the course of the dissociation energy along different periods, comparing for instance the oxides and sulphides of the fourth group with each other, the spectra of these molecules being known better than of those in any other period. It can be seen from Table II that the energy of dissociation decreases as we proceed along a row or go down along a column. This means that the bond energy runs parallel to the field strength, with no regard to the polarity of the molecule. From CO to PbO

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* The departure of GaO from CaO is much more pronounced than that of AlO from MgO, but we believe that the value of CaO is slightly too high because it cannot be higher than that of MgO.

TABLE II.

	C	Si	Ge	Sn	Pb
O	~10	7·8	7·3	5·8	4·3
S	7·8		5·7	5·5	4·7
Se	4·2				

the bond energy decreases, whereas the polarity increases, while from CO to CSe both decrease together. It has been pointed out already elsewhere[10] that such a course is not compatible with a theory in which each single electron contributes independently towards the energy of formation. In such a theory the wavemechanical interaction of the electrons (other than that represented by a simple screening effect), is neglected and the bonding effect is due to the degeneracy of the nuclear fields. But the polarity is another expression for the dissymmetry of the nuclear fields and this theory should predict the bond energy and the polarity to run together. That is another instance again in favour of the electron pair-bond theory of valency.

The difference between the two interpretations of the method of molecular orbitals shows itself in polyatomic molecules as the difference of non-localised and localised bonds. With the exception probably of hydrides and certainly of aromatic compounds, where non-localised electrons are present, brought about by hybridisation of the localised bonds, and where they just produce the specific aromatic character, the pair-bond theory of valency leads to localised bonds as a result of the wavemechanical interaction, mentioned above, while its neglection leads to non-localised bonds, and this neglection is necessary if the energy of formation of a molecule shall be conceived as the sum of the contributions of individual independent electrons. We have shown elsewhere,[11] that a close correspondence exists among the ω values known from infra-red and Raman spectra of certain polyatomic molecules and those of the constituent diatomic radicals, known from band spectra. Though the number of such instances known is not very large at the present moment, we believe that the coincidences are not fortuitous and that they therefore favour the conception of localised bonds. We have further tried to follow this correspondence in respect of dissociation energies. In the case of the chlorides and oxychlorides of di- and tetravalent sulphur a correlation between the bond energies could be established by their photo-dissociation[12] and it was found, that, *e.g.*, the S = S bond has the same energy in polyatomic molecules as is obtained from the band spectrum of S_2. An

extension of such a correlation to other molecules is not so conclusively possible for want of sufficient and reliable data. In spite of this we should like to point out certain interesting features among the available instances. The values of dissociation energy obtained from the usual linear extrapolation of vibrational levels are by no means satisfactory in many cases, if taken individually. But there seems to be little doubt that the errors thus introduced cancel out, probably because they are in the same direction, when we correlate the products of dissociation in different electronic states of one and the same molecule to the terms of the constituent atoms. For our present purpose we shall have to use individual values which therefore are not absolutely correct and therefore are expected to differ from the thermochemical values.

Among the few instances, which are available for such a comparison there are some, which exhibit a close relation between the bond energies of the diatomic radical molecule and the saturated chemical molecule. Denoting by D_0 values from the dissociation energy derived from band spectra and by D_T such from thermochemical measurements (both in volts), we collect them in the following table :—

TABLE III.

	D_0	D_T	D_T'
AgO	1·8	$1/2\ D_T\ (Ag_2O) = 1·9$	
PbCl	3·3	$1/2\ D_T\ (PbCl_2) = 3·4$	$1/4\ D_T\ (PbCl_4) = 2·1$
BiCl	3·6.	$1/3\ D_T\ (BiCl_3) = 3·3$	
BiBr	2·7	$1/3\ D_T\ (BiBr_3) = 2·4$	
SbF*	~4	$1/3\ D_T\ (SbF_3) = 4·6\ (5·6)$	
SO	5·1	$1/2\ D_T\ (SO_2) = 5·4$	$1/3\ D_T\ (SO_3) = 4·7$
SeO	4·2	$1/2\ D_T\ (SeO_2) = 4·5$	$1/3\ D_T\ (SeO_3) = 3·7$

* For the thermochemical energy of formation two values exist in literature, which lead to 4.6 and 5.6 volts, respectively (cf. Mellor).

It is interesting to note, that where a comparison is possible, D_0 agrees better with the thermochemical value derived from the molecule with lower valency than from that with maximal valency of the central atom. The best known example for such a behaviour is of course CO, where D_T (CO)

gives 235 K.cal./mol., $\frac{1}{2}$ D (CO_2) 181 K.cal./mol. This is connected with the fact, that the D_T values for such molecules with maximal valency are not bond energies at all, *i.e.*, do not refer to the *adiabatic* dissociation by excitation of the vibrational levels, because the ground level of a molecule like CO_2 or SO_3 is not formed by the combination of unexcited CO or SO_2 and unexcited O atom. This is clear from the diamagnetic character of these molecules and absorption spectra indicate, that the halides of the maximal and minor state of values are in a similar relation[12] at least from the fourth group of the periodic system onwards. It cannot be said for certain whether the ground level of a molecule like SO_3 involves excited oxygen atoms or excited SO_2 molecules, but since the pair-bond view would be better satisfied by the splitting off of the original s^2 group of S, the above relation appears again to favour the latter standpoint.

It is further interesting to note, that in cases like AsO and SbO the values $\frac{1}{3}$ D_T (As_2O_3) = 7.6 and $\frac{1}{3}$ D_T (Sb_2O_3) = 7.3 volts agree better with the dissociation energy of those terms of AsO and SbO in which the odd electron is already partly removed. The dissociation energy of the ground level of AsO is 5.0, that of the B $^2\Sigma$ term is 6.1 ; the corresponding figures for SbO are 5.3 and 6.2 volts. The energies of formation of N_2O_3 and P_2O_3 are not certain, but we may expect the same relation there also.

Conclusions.

The original interpretation of the method of molecular orbitals as a theory of valency, in which the single electron possesses bonding power was based on the assumption that non-premoted electrons are bonding and premoted ones are anti-bonding or non-bonding. This assumption is not the outcome of any requirements of theory but is an empirical postulate, which seeks justification in experimental facts. Earlier attempts at correlation between the electronic levels of molecules and the energy states of the constituent atoms indeed appeared to lend support to this assumption. Later investigations have, however, shown that completely different correlations are possible and are absolutely necessary to satisfy the experimental facts. For example, in a molecule like BeO the stable triplet term, which should arise from unexcited atoms according to the older correlation, is not found and by the correlation of certain excited terms to anomalous terms of the metal atom it is shown, that a non-premoted odd electron in the configuration of the ground level lowers its dissociation energy. Similar remarks apply to the types BeF and NO and the new correlation of molecular terms to atomic states from the pair-bond view is shown to be satisfactory without exception in a larger number of molecules of these three classes, recently.

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These three types represent molecules with free valencies and indeed just in such molecules the difference of the two view-points must become apparent. For other such molecules with free valencies, whose band spectrum is investigated in detail, *i.e.*, for the oxides of the third and the halides of the fourth group of the periodic system, only one example of each, *i.e.*, AlO and SnCl, was originally available. We have now shown in the present paper, that the correlation according to the pair-bond theory of valency holds also for other molecules of this type and appears to be generally valid. *All this evidence*, concerning the band spectra of oxides and halides of the second, third, fourth, and fifth groups of the periodic system *is definitely against the postulate of the identification of premoted and non-premoted with non-bonding and bonding electrons*. On the other hand, such a satisfactory correlation from the pair-bond view necessitates a revision of the theory of valency, based on the results of band spectroscopy.

From the purely experimental point of view an interpretation of the method of molecular orbitals as electron pair-bond theory of valency is furthermore supported by the course of the bond energies in the periodic system. The near relationship shown at the present moment in a few instances, between the bond energies of diatomic radical molecules with those of polyatomic chemical molecules, in which however the maximal valency does not manifest itself, also points in this direction. The close correspondence between the ω values of polyatomic molecules and of their radicals in the ground state in many cases and in the excited states also of some polyatomic molecules whose spectra have been recently investigated,[11] indicate a localisation of bonds which is the direct outcome of the pair-bond theory of valency. Further evidence in favour of this view is afforded by absorption spectra and photo-dissociation of halides and oxyhalides of di- and tetravalent sulphur, selenium, and tellurium, all of which show almost a rigorous constancy of each bond energy. To our mind, therefore, all this spectroscopical evidence undoubtedly bears out the electron pair-bond theory of valency.

REFERENCES.

1. H. Lessheim and R. Samuel, *Phil. Mag.*, 1936, 21, 41 and earlier.

2. R. S. Mulliken, *Rev. Mod. Phys.*, 1931, 4, 1.

3. H. Lessheim and R. Samuel, *Z. Phys.*, 1933, 84, 637; 1934, 88, 276.

4. M. L. Guernsey, *Phys. Rev.*, 1934, 46, 114; E. Miescher and M. Wehrli: *Helv. Phys. Acta.*, 1934, 7, 331.

5. H. Lessheim and R. Samuel, *Ind. Journ. Phys.*, 1936, 10, 7.

6. R. K. Asundi and R. Samuel, *Proc. Ind. Acad. Sci.* (Bangalore), 1936, 3, 346.

7. A. C. Datta, *Z. Phys.*, 1932, **78**, 486.

8. D. Coster and F. Brons, *Proc. K. Amst. Ac.*, 1935, **38**, 961; F. Brons, *Physica*, G. Scheibe and J. Franck, 1935, **2**, 1108; B. Rosen, M. Desirant and J. Duchesne, *Phys. Rev.*, 1935, **48**, 916.

9. B. Rosen, *Z. Phys.*, 1927, **43**, 69.

10. H. Lessheim and R. Samuel, *Proc. Ind. Acad. Sci.* (Bangalore), 1935, **1**, 623 (Section x ff.).

11. R. K. Asundi and R. Samuel, *Proc. Ind. Acad. Sci.* (Bangalore), 1935, **2**, 30; R. K. Asundi, Mohd. Jan Khan and R. Samuel, *Nature*, 1935, **136**, 642.

12. R. K. Asundi and R. Samuel, *Proc. Phys. Soc.* (London), 1936, **48**, 28; Mohd. Jan Khan and R. Samuel, *Ibid.*, (in press); S. L. Hussain and R. Samuel, *Curr. Sci.*, 1936, **4**, 734.