Informations - Informationen - Informazioni - Notes

STUDIORUM PROGRESSUS

The Valence-State Energy of the Tetravalent Carbon Atom

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1. *Introduction*

The purpose of this article is to examine the structure of a few simple organic molecules from the energetic aspect, particular reference being made to the question of the energy of the valence state of tetravalent carbon and its derivation from known thermochemical data. A systematic treatment of this problem from the thermochemical point of view seems never to have been undertaken, perhaps because the true situation has for long been obscured by uncertainty regarding the values to be assigned to a number of thermochemically important quantities, and partly because the type of reasoning involved is one not normally encountered in thermochemistry. The present paper does not claim to be more than a step towards the solution of this problem, but certain conclusions which it is possible to draw from observational data may prove of value in checking physical theories.

In conformity with the wave-mechanical picture of the chemical bond, the true or natural energy of a bond may be regarded as a specific property of the bond *in the unperturbed molecule*, like, for example, the bond length or the stretching force constant. This energy we will term, after R. S. MULLIKEN, the *intrinsic bond energy*. It is the energy liberated when two atoms *in their appropriate valence states* unite to form a bond. The valence state of an atom in combination may be defined as the hypothetical state in which the free atom would find itself if its chemical bonds could be ruptured without change in the electronic configuration. In as much as the resultant electronic configuration is not that of the ground state, atoms in their valence states possess surplus energy, that is they are *excited*. The fundamental situation is not in the least affected by the fact that valence states are not spectroscopically observable with the free atoms. For theoretical treatment it is frequently convenient to regard valence states as mixtures of observed atomic states.

In order to avoid confusion, it is necessary from the outset to be clear about the fact that *intrinsic* bond energies are not the same as the bond energies ordinarily spoken of. The latter are thermochemically defined so as to make the sum of the bond energies of a molecule equal to the atomic heat of formation of the molecule, that is, the heat liberated on its formation from free atoms in their ground states. Since the atomic heat of formation is also equal to the sum of the intrinsic bond energies *less* the sum of the energy of the valence states of all the atoms involved, that is, to

$$\Sigma E - \Sigma V$$

(where E represents the intrinsic energy of a bond and V the internal energy of an atom in its valence state), it is seen that the intrinsic bond energies are in general *larger* than thermochemical bond energies. The *inter-atomic* energy is thus larger than commonly supposed, but the increase is compensated for by a loss in *intra-atomic* energy. Logically, it is the intrinsic bond energy rather than the thermochemical bond energy which is related to other bond properties such as the bond length and force constant[1], and it is the intrinsic bond energy which concerns us here.

Turning our attention to diatomic molecules, it is seen that with the rupture of the bond joining the atoms, the latter are able to fall to their ground states. Consequently, for a molecule AB, the measured dissociation energy, $D(\mathrm{AB})$, is a net effect only, and does not provide the value of $E(\mathrm{A{-}B})$, the intrinsic energy of the bond. The actual relationship is given by

$$D(\mathrm{AB}) = E(\mathrm{A{-}B}) - V(\mathrm{A}) - V(\mathrm{B}).$$

Since the intra-atomic energy is entirely regained during the process of dissociation, the dissociation energies alone tell us nothing concerning the valence states of the atoms in the case of diatomic molecules.

With polyatomic molecules, however, the situation is different. Here, with the rupture of an electron-pair bond between two atoms, one at least of the two atoms is obliged to remain in the appropriate valence state, since it remains chemically linked with other atoms. In principle, therefore, it is possible to gain information regarding valence states from the dissociation energies of *polyatomic* molecules, provided the experimental data is correctly interpreted. The position is however rendered more complicated by the fact that, when one bond in a molecule is ruptured, the neighbouring bonds are inevitably affected, even if only slightly. It is thus in general necessary to make allowance for a number of small energetic effects, and this, with our present state of knowledge, tends to become the most difficult and least satisfactory aspect of the matter. It constitutes a major factor in determining the accuracy of estimations of this kind, and a strong reason for confining attention to simple polyatomic molecules.

Our knowledge of dissociation energies for polyatomic molecules is still in an exceedingly incomplete state, and much information which would be very useful in throwing light on the positions of valence states is unfortunately still lacking. However, enough data for certain organic compounds exist to provide at least an intelligent idea of the energy level of the valence state of carbon from several different lines of reasoning. Before proceeding to illustrate this with examples, it would be both useful and instructive to make a brief historical survey of the viewpoints which have been held concerning the true nature of the valence state.

2. *Past Ideas concerning the Nature of the Valence State*

It appears first to have been recognized 20 years ago by MECKE[2] that the energy required to promote a carbon atom to its tetravalent state must affect the bond energies in organic compounds. Using values then current for dissociation energies, he argued that because the process

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[1] For a perfect treatment of intrinsic bond energies, it would be necessary to separate out the much smaller forces between non-bonded atoms. For interrelating bond properties, however, it is very questionable whether this would be worth while, since not only will these forces affect the energies of neighbouring bonds somewhat, but also their lengths and force constants in comparable manner.

[2] R. MECKE, Nature *125*, 526 (1930).

$$HCO \rightarrow CO + H$$

liberates 4 kcal instead of absorbing 107 kcal in conformity with the process

$$H_2CO \rightarrow HCO + H,$$

the excitation of the $C{=}O$ molecule to $={C}{=}O$ (containing tetravalent carbon) absorbs 111 kcal. A like argument involving $D(OC{=}O)$ provided a similar figure. Mecke also forecast that the energy required to rupture the second C—H bond in methane would be much less than that required to rupture the first[1], on the grounds that in methylene, free CH_2, the carbon is divalent.

These ideas were developed on the physical side by Heitler and Rumer[2] and on the chemical by Norrish[3], who recognized that the ^3P state of carbon is an s^2p^2 state, and possesses only two unpaired electrons for bond-formation, whereas for carbon to appear tetravalent one of the s electrons must be promoted to the vacant p orbital to give an sp^3 state. The lowest atomic state answering this description is the ^5S state, and the employment of this state instead of the ground state as the basis of the respective calculations constituted a definite advance. At the time, the position of the ^5S state was generally believed to be nearer to the ground state than is now known to be the case.

Of the various subsequent theoretical treatments of polyatomic molecules, those by Van Vleck[4] (to whom the term *valence state* is due) and by Mulliken[5], who extended the treatment to a large number of atoms other than carbon, deserve special mention. In the Van Vleck treatment, the importance of electron spin and bond direction is emphasized. According to this viewpoint, the correct reference state for carbon in methane is not the ^5S state alone, but a mixture of all the sp^3 states (six in number), since, apart from the fact that the ^5S atom does not direct its four valence electrons tetrahedrally, the spins of the latter are all parallel, a restriction which is not to be presumed operative in chemically bound carbon. In this treatment, the spins are instead presumed to be symmetric. A corresponding linear combination of all the six sp^3 states leads to a promotional energy of 7–8 eV for the carbon atom in its valence state. The result is surprisingly high when it is remembered, for example, that the ionization potential of carbon is only 11·265 eV and that, experimentally, the energy of the C—H bond is of the order of 4 eV.

A revision of Van Vleck's treatment has been undertaken by Voge[6], who attempted to remove certain imperfections by employing a different combination of s^2p^2, sp^3, and p^4 atomic terms. This again yielded the value 7 eV for the valence state in methane, but the question of a possible reduction through resonance was raised. However, it is doubtful if the level could be depressed appreciably in this way. Apart from the evidence which has been accumulating in recent years against resonance of this kind, Coulson[7] has calculated that delocalization of the bonding electrons in methane is very small.

In order to suggest a possible explanation for the difficulty created by the theoretical value 7 eV—it is quite twice as large as that permissible according to observational data[1]—it might be remarked here that, energetically speaking, once a carbon atom has become excited to the ^5S state by the promotion of an s electron to a p orbital (to make the formation of four electron-pair bonds possible), further excitation is only to be expected as long as the gain in intrinsic bond energy more than compensates for the energy absorbed by excitation. This is in accordance with the inviolable principle that a molecule will adjust itself so as to make its total energy a minimum. It need not be surprising, therefore, if this point is reached a long way below that demanded by the symmetric electron-spin configuration. A treatment which subordinated energetic considerations to those of electron spin and bond direction, important as these are, could thus never be perfect. This fact has apparently been recognized by Nordheim-Pöschl[2], who, in a completely different theoretical approach to simple organic molecules, excludes at the outset all states higher than the 5s as energetically too high to play a significant rôle in chemical bonding, and attempts to account for the directional properties of the tetravalent carbon atom in terms of a combination of the ^3P and ^5S states. No estimate of the energy of the valence state is given, but, in view of what follows, it would be well worth investigating whether this kind of treatment could be developed to give a picture conformable to experiment.

During the decade following 1936, the matter was not carried much further. One of the main reasons for this was doubtless the insufficiency of reliable experimental data by means of which physicists could check and build upon their theories. The question of the valence state of carbon was re-examined in 1946 from the experimental angle by Long and Norrish[3], who found that the evidence pointed unequivocally to an energy level of ~65 kcal (~2·8 eV). This it was impossible to link up with the 7 eV provided by the Van Vleck-Voge treatment, but was in reasonable agreement with the estimate ~3·16 eV for the then unobserved ^5S level by Ufford[4]. The experimental facts accordingly pointed at the time to the older viewpoint, according to which the valence state was identified with the ^5S state, as being the correct one. However, the subsequent observation of the ^5S level at 4·16 eV or 96·4 kcal by Shenstone[5] showed Ufford's estimate to be misleading. The true position thus turns out to be less simple than was formerly supposed, and it is now possible to state with some confidence that the valence state of tetravalent carbon is situated not above the ^5S level, but *below*[6] it. The recognition of this fact is a step forward towards placing the whole subject on an energetically sound footing, and should be of assistance to the theoretical physicist.

One other completely different approach must be mentioned which has particular reference to diatomic molecules. It has long been recognized that linear Birge-Sponer extrapolations—which depend upon the molecular constants at the potential minimum—lead to dis-

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[1] R. Mecke, Z. Elektrochem. *36*, 595 (1930).

[2] W. Heitler and G. Rumer, Z. Physik *68*, 12 (1931).

[3] R. G. W. Norrish, Trans. Faraday Soc. *30*, 103 (1934).

[4] J. H. Van Vleck, J. Chem. Phys. *2*, 20, 297 (1934). – J. H. Van Vleck and A. Sherman, Rev. Modern Phys. *7*, 167 (1935).

[5] R. S. Mulliken, J. Chem. Phys. *2*, 782 (1934).

[6] H. H. Voge, J. Chem. Phys. *4*, 581 (1936); *16*, 984 (1948).

[7] C. A. Coulson, Quart. Rev. Chem. Soc. *1*, 165 (1947).

[1] That the figure 7 eV is much too high, may be readily seen from a consideration of acetylene and its halogen derivatives. The ground state of these molecules is unquestionably $X{-}C{\equiv}C{-}X$, but this would be stable relative to $X{-}C{-}C{-}X$ only as long as the difference in the bond-energy sum for the two structures exceeded the sum of the promotional energies of the two carbon atoms. A figure even approaching 7 eV for each atom is accordingly seen to be excluded. See L. H. Long, Z. Elektrochem. *54*, 79 ff. (1950).

[2] G. Nordheim-Pöschl, Ann. Physik [v], *26*, 258, 281 (1936).

[3] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. A *187*, 337 (1946).

[4] C. W. Ufford, Phys. Rev. [ii], *53*, 568 (1938).

[5] A. G. Shenstone, Phys. Rev. [ii], *72*, 411 (1947).

[6] L. H. Long, Z. Elektrochem. *54*, 77 (1950).

sociation energies which are normally considerably in excess of the true value. PAULING[1] has made the reasonable assumption that the extrapolated values correspond to the energies required to dissociate the respective molecules into atoms *in the valence states* relevant to the molecule under consideration. (In the language employed in the introduction, this is tantamount to saying that the extrapolated value for the dissociation energy constitutes an estimate of the intrinsic bond energy of the molecule.) An alternative procedure is to carry out a linear extrapolation of the *lowest* vibrational levels (zero lines). The two methods normally give similar, but not identical, values. As the assumptions involved hold to a first approximation only, the accuracy of the figures obtained for the valence states will again be somewhat limited. This line of approach has not so far been applied to tetravalent carbon, but has been employed for estimating the level of the divalent state and the levels of the valence states of oxygen and nitrogen[2].

3. *Valence States and Dissociation Energies*

The significance of the intra-atomic energies possessed by atoms when in their valence states is well illustrated by a study of the experimental values for the dissociation energies of individual chemical bonds in the case of *polyatomic* molecules. These dissociation energies reflect the necessity for taking the intra-atomic energies into account when estimating true or intrinsic bond energies, as is particularly well illustrated in the case of C–H and C–C bonds.

It will be convenient in the following to represent the energy of a valence state by the symbol V. Thus $V(\mathrm{C^{IV}})$ represents the energy of a carbon atom in its tetravalent state. To be strictly accurate, the type of hybridization should be indicated, as, for example, in the symbol $V(sp^3\ \mathrm{C^{IV}})$, since slight differences in energy will exist, according to whether the hybridization is sp^3 (tetrahedral), as in CH_4 and CCl_4, or sp^2 (trigonal) as in C_2H_4 and C_6H_6, or sp (digonal) as in C_2H_2 and CO_2. Theoretically, at least, the difference in energy levels for these hybridized states is quite small. Experimentally, it is doubtful whether it is yet possible to distinguish between them.

The heat of atomization of graphite will here be taken as 125·0 kcal at 0°K. This is an accurate figure derived from a spectroscopic study of carbon monoxide, and a study of the evidence from other sources indicates that it is the most probable value[3]. In any case, the correct value is almost certainly within about 10 kcal of this figure[4]. The heat of atomization of hydrogen is known with accuracy to be 51·6 kcal at 0° K. The valence state and the ground state of hydrogen will here be assumed to be virtually the same. There are here no low-lying atomic states which one would expect to contribute to the bonding and a Birge-Sponer extrapolation calculated from the molecular constants ω_e and $\omega_e\,x_e$ for H_2 indicates that the difference between the states in question is negligible. On account of the non-linearity of the $\Delta G - v$ curve for H_2, however, extrapolation of the lowest vibrational levels leads to a definite, though relatively small, valence energy. The point is worthy of mention, as the discrepancy between the two extrapolation procedures is indicative of their limited reliability.

From a far-reaching regularity in the accurately known heats of formation of the straight-chained paraffins at 0° K[1], it can be demonstrated that the energy of the C–C bonds is constant to within 0·1 kcal. The C–H bond varies only comparatively slightly in strength, that in methane being slightly stronger than the average values for the higher paraffins. The values for the intrinsic bond energies (E values) are given below (in kcal) for the C–H bond in methane and the C–C bond in ethane:

$$E(CH_3 - H) = 86{\cdot}85 + \tfrac{1}{4}\,V(\mathrm{C^{IV}});$$
$$D(CH_3 - H) = 101{\cdot}5 \pm 1.$$

$$E(CH_3 - CH_3) = 59{\cdot}9 + \tfrac{1}{2}\,V(\mathrm{C^{IV}});$$
$$D(CH_3 - CH_3) = 84{\cdot}3 \pm 2.$$

The experimental dissociation energies[2] of the corresponding bonds at 0° K (D values) are placed alongside for comparison. For aliphatic hydrocarbons, other measured dissociation energies are similar, namely about 100 kcal for D(C–H) and about 80 kcal for D(C–C). It is immediately obvious that the energy of the valence state of carbon must be considerable if the figures are to bear relationship. If, *as a first approximation*, one equates the D values with the intrinsic bond energies, the values derived for $V(\mathrm{C^{IV}})$ are 58·6 and 48·8 kcal respectively. The matter is not so simple, however, as this procedure neglects the *energy of reorganization* of the methyl radical on its formation from methane or ethane.

The factors entering into this energy of reorganization are change in energy of the three unruptured C–H bonds and change in the internal energy of the carbon atom. The latter will at all events be small, even if the hybridization changes all the way from sp^3 to sp^2, and will be associated with a small but not negligible increase in the energy of the three remaining bonds due to increase in their s character. That energy will be liberated but will not be more than a few kilocalories, is indicated by the fact that the C–H bond in ethylene, where the bonding is sp^2, has properties which differ only slightly from those of the C–H bond in methane. A study of bond properties by WALSH[3], namely bond energies, bond lengths and force constants, has indicated that the C–H bond in ethylene is the stronger by only about 2 kcal. It follows that the above estimate for the valence states, although only approximate, will be of the right order of magnitude. In point of fact, the C–H bond in the free methyl radical may well be intermediate in character between those in methane and ethylene.

Any liberation of energy through reorganization of the methyl radicals on their formation would mean that the observed dissociation energies are lower than the actual intrinsic bond energies. Consequently the figures 58·6 and 48·8 kcal already derived represent lower limits for the valence energy of tetravalent carbon. (The

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[1] L. PAULING, Z. Naturforsch. *3a*, 438 (1948).

[2] L. PAULING, Proc. Nat. Acad. Sci., U.S. *35*, 229 (1949). – L. PAULING and W. F. SHEEHAN (Jr.), *ibid.*, p. 359.

[3] L. H. LONG, Proc. Roy. Soc. A *198*, 62 (1949).

[4] A much higher value around 170 kcal has frequently been proposed, but there is no objection-free evidence in support of it, and the weight of the evidence indicates that it can be excluded. From independent considerations, PAULING and SHEEHAN (*loc. cit.*) also exclude this value. That PAULING and SHEEHAN favour a value somewhat higher than 125 kcal is due to their assumption that the carbon in the ground state of CN and the lowest triplet state of CO is in the divalent (and not tetravalent) state. See later and L. H. LONG, Research, London *3*, 291 (1950).

[1] E. J. PROSEN, K. S. PITZER, and F. D. ROSSINI, J. Research National Bur. Standards, U. S. *34*, 403 (1945).

[2] The figure for $D(CH_3$—H) is that given by G. B. KISTIAKOWSKY and E. R. VAN ARTSDALEN, J. Chem. Phys. *12*, 469 (1944), after correcting for an improved value of D(HBr) involved in the calculation [cf. L. H. LONG, Proc. Roy. Soc. A *198*, 65 (1949)]. The figure for $D(CH_3$—$CH_3)$ follows from this.

[3] A. D. WALSH, e. g., J. Chem. Soc., *1948*, p. 398; Discussions Faraday Soc. *2*, 18 (1947). The bonding in free CH_3 is specifically considered on p. 21 of the latter article.

difference in the figures implies that the energy of reorganization is 2·45 kcal greater when it is formed from ethane than when it is formed from methane. This can be readily accounted for when it is reflected that the C–H bond energy in methane is 0·8 kcal stronger than in ethane, as may be shown directly from the heats of formation of these two compounds.)

Having now a lower limit for the energy of the valence state, an upper limit must be sought. This is provided by the position of a triplet state of ethylene which has been experimentally fixed at 72–74 kcal above the ground state by LEWIS and KASHA[1], who also identify this triplet state with the symmetrical biradical

$$-CH_2-CH_2-$$

obtained by removing two hydrogen atoms from ethane. If, in first approximation, it is assumed that the intrinsic energies of the bonds it contains are identical with those in the ethane molecule, it can be shown that the sum of the intrinsic energies of the two bonds of the ethane molecule which are regarded as ruptured on the production of the biradical is related to the forementioned experimental figure, 73 ± 1 kcal, by an algebraic sum involving only the heats of formation of ethane and ethylene and the dissociation energy of the hydrogen molecule, all of which are accurately known. The details of this calculation are given elsewhere[2], and will not be repeated here. The procedure leads to 70·2 kcal as an estimate for $V(C^{IV})$, the valence energy of carbon.

Again the method is only approximate. In particular, the assumption that all the bonds in the biradical $-CH_2-CH_2-$ are identical with the corresponding bonds in ethane neglects the possibly important mutually repulsive effect of the two unpaired electrons. Such would considerably weaken the C–C link, thus destabilizing the biradical and reducing the estimate of $V(C^{IV})$. That this factor is indeed important and exceeds any stabilizing effects due to reorganization of the biradical, is indicated by the fact that the energy required for the process

$$C_2H_5 \rightarrow -CH_2-CH_2- + H,$$

namely 109 kcal, is several kilocalories more than the value for $D(C_2H_5-H)$, namely 98 kcal. The value of $V(C^{IV})$ provided by this procedure, namely 70·2 kcal, may thus be regarded as an upper limit for the energy of the valence state.

The true value may therefore be supposed to lie somewhere between 58·6 and 70·2 kcal. Other calculations of this sort based on experimental dissociation energies provide very similar values. All suffer from the necessity of making approximating assumptions at some point or other, and it is not at present possible to express the energy of the valence state with greater precision. It is to be noted that these estimates are all linked with the heat of atomization of graphite in such a way that any increase in the value of the latter involves a corresponding decrease in the energy of the valence state, that is to say, the heat of atomization of graphite to free atoms in the tetravalent state remains constant at ~190 kcal per gram-atom, whatever the true value for the heat of atomization to atoms in their ground state.

4. *Change in Valency*

The foregoing examples are confined to cases in which no changes of valency are involved. On the rupture of a double bond, the additional possibility of change in valency must be considered, if by pairing off the two odd electrons one (or both) of the atoms is able to reduce its valency by two. This article would not be complete without the discussion of at least one such case. Carbon dioxide provides a convenient example.

The energy required to dissociate one of the bonds in carbon dioxide can be very accurately calculated from the difference in the heats of formation of carbon dioxide and carbon monoxide at 0° K. The value thus obtained for $D(O{=}CO)$ is 125·35 kcal. This figure is very much less than the intrinsic energy of the bond because of the valence energy of the oxygen atom, which is of the order of 0·74 eV or 17 kcal[1], and the energy of reorganization of the CO radical on passing to the ground state of carbon monoxide. Two factors contribute to make the latter quantity very considerable, namely marked increase in strength of the unruptured C=O bond, as witnessed by the decrease in length and increase in force constant, and a drop in the internal energy of the carbon atom as it passes from the tetravalent to the divalent state, there being no question that the $^1\Sigma$ ground state of carbon monoxide contains no unpaired electrons. The intrinsic energy of the C=O bond in carbon dioxide is therefore

$$125{\cdot}35 + V(O^{II}) + \Delta E + V(C^{IV}) - V(C^{II}),$$

where ΔE represents the difference in intrinsic bond energy of the C=O bond in carbon dioxide and carbon monoxide. Since the atomic heat of formation of carbon dioxide is 336·1 kcal, the intrinsic bond energy is also equal to

$$\tfrac{1}{2}\,(336{\cdot}1) + \frac{1}{2}V(C^{IV}) + V(O^{II}),$$

so that, by equating the two expressions and substituting the experimental value 1·73 eV or 40 kcal for $V(C^{II})$[2],

$$\tfrac{1}{2}\,V(C^{IV}) = 82{\cdot}7 \text{ kcal} - \Delta E. \qquad (1)$$

In order to determine the value of ΔE, a knowledge of the intrinsic bond energies in CO and CO_2 is required. That in CO can be calculated by adding the forementioned valence energies for divalent carbon and oxygen to the dissociation energy of CO, namely 9·14 eV. The result 11·61 eV, is in only fair agreement with the value obtained by PAULING and SHEEHAN[3] by extrapolation of the lower vibrational levels of CO, namely 11·23 eV, which is likewise an approximate figure. [The value adopted for $D(CO)$ is not quite certain, but had one of the alternative higher values been selected, the discrepancy in the two estimates of the intrinsic bond energy would have been markedly greater.] The best we can do is to take the mean of the two figures, namely 11·42 eV or 263 kcal.

The intrinsic bond energy in CO_2 can be estimated by considering the dissociation energy of one of the bonds for a process in which the carbon remained in the tetravalent state. The unruptured bond in the $>C{=}O$ radical would simultaneously readjust itself with the appearance of the two unpaired electrons, and the final result (with maintenance of tetravalence for the carbon) would be a carbon monoxide molecule not in the Σ ground state, but in an excite Π state. The lowest of these is the $a\,^3\Pi$ state, which answers the description perfectly. In this case, increase in the bond length and decrease in the force constant indicate a considerable decrease in strength of the unruptured C=O link.

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[1] G. N. LEWIS and M. KASHA, J. Amer. Chem. Soc. *66*, 2100 (1944).

[2] L. H. LONG, Z. Elektrochem. *54*, 79 (1950).

[1] L. PAULING, Proc. Nat. Acad. Sci., U. S. *35*, 229 (1949).

[2] L. PAULING and W. F. SHEEHAN (Jr.), Proc. Nat. Acad. Sci., U. S. *35*, 359 (1949).

[3] L. PAULING and W. F. SHEEHAN, *loc. cit.*

The excitation energy of the $a\,^3\Pi$ state being accurately known from spectroscopic data, the energy required for the process

$$CO_2 \rightarrow O(^3P) + CO(a\,^3\Pi)$$

can be calculated thermochemically to be 264 kcal. The extrapolation procedure of PAULING and SHEEHAN indicates an intrinsic bond energy of 146 kcal for the $a^3\Pi$ state of CO, so that $(146 - x)$ kcal must here be allowed for the reorganization energy of the CO radical, where x is the intrinsic energy of the C=O bond in carbon dioxide. Accordingly, since the dissociation energy will differ from the intrinsic energy by an amount equal to the change in internal energy of the fragments,

$$264 = x - V(O^{II}) - (146 - x),$$

from which equation, after substitution of the previously mentioned value 17 kcal for $V(O^{II})$, x is seen to be 213·5 kcal. This value for the intrinsic bond energy in CO_2 is perfectly reasonable from the point of view of bond properties. It is seen to be 49·5 kcal less than that in the ground state of carbon monoxide. This provides the figure for ΔE required in equation (1), from which $V(C^{IV})$ is seen to be approximately 66 kcal, in good agreement with the previous estimates.

Alternatively, $V(C^{IV})$ can be estimated directly from the intrinsic bond energy in CO_2, for which we have derived the approximate figure 213·5 kcal. This is numerically equivalent to one-half the atomic heat of formation of CO_2 plus the valence energy of oxygen plus one-half the valence energy of carbon, that is, to $(\frac{1}{2} \times 336{\cdot}1) + 17 + \frac{1}{2}V(C^{IV})$. This procedure provides the figure 57 kcal for $V(C^{IV})$.

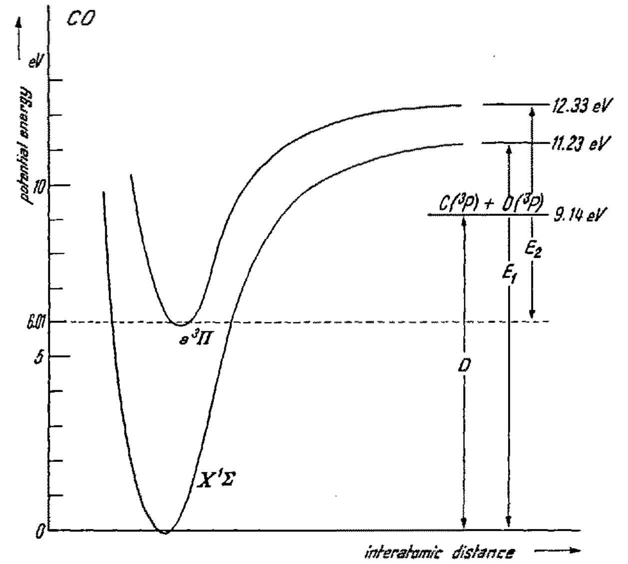

Fig. 1. – Extrapolated potential-energy curves (schematic) of the ground state and lowest excited state of CO. The dissociation limits are linear convergences of the lowest few vibrational terms. These curves differ from those usually given. For low vibrational energy, they will coincide with the observed curves, but near the dissociation limits will deviate considerably from the "true" curves (which are not in any case observable in this region), as interaction with discrete atomic terms of the dissocation products is intentionally neglected. The dissociation limits obtained in this way do not correspond to combinations of atomic terms, but to combinations of atoms in hypothetical valence states. The method provides direct—though approximate—estimates of the *intrinsic* bond energies for the ground states of the molecule, which energies are here indicated as E_1 and E_2 respectively. The energy level of the separated atoms in their ground states, that is, the dissociation energy, D, is here shown at 9·14 eV. These quantities are related to the valence energies as follows:

$$E_1 - D \approx V(C^{II}) + V(O^{II});$$
$$E_2 + 6{\cdot}01\text{ eV} - D \approx V(C^{IV}) + V(O^{II}).$$

Yet another method of estimating $V(C^{IV})$ is by means of linear extrapolations of the lower vibrational levels of the $X^1\Sigma$ and $a^3\Pi$ states of CO. If, as there is good reason to believe, these are respectively derived from divalent (s^2p^2) and tetravalent (sp^3) carbon, the latter state should give a linear convergence at a point some distance above that of the former. This is in fact observed, (see fig. 1), the values being 11·23 and 12·33 eV respectively above the ground level[1]. The difference, 1·10 eV, gives the difference in level between the tetravalent state and the divalent state. Taking the level of the latter as 1·73 eV[1], that of the former becomes 2·83 eV or 65 kcal.

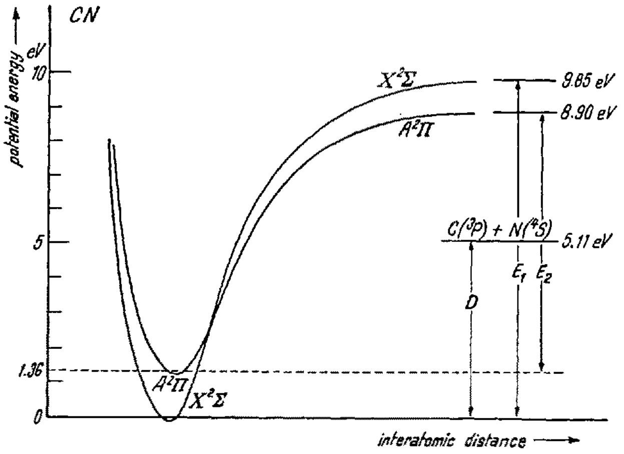

Fig. 2. – Extrapolated potential-energy curves (schematic) of the ground state and lowest excited state of CN. The extrapolations are of the same type as those for the states of CO in figure 1. The energy level of the separated atoms in their ground states is here shown at 5·11 eV[3]. (The origin of the $A^2\Pi$ state is the revised level given by Herzberg and Phillips[4].) The extrapolated curves cross, and in this instance—in contrast to the case of CO—it is the ground state which is derived from tetravalent carbon and the excited state from divalent carbon. E_1 and E_2 are the respective intrinsic bond energies of the two states, and are related with the valence energies as follows:

$$E_1 - D \approx V(C^{IV}) + V(N^{III});$$
$$E_2 + 1{\cdot}36\text{ eV} - D \approx V(C^{II}) + V(N^{III}).$$

The reasonable agreement between the various estimates is further confirmation that the carbon in the $a\,^3\Pi$ state of CO is indeed tetravalent. This fact has an important bearing on the selection of the correct value for $D(CO)$. On deducting the respective valence energies from the points of linear convergence of the $X\,^1\Sigma$ and $a\,^3\Pi$ states, both states agree in indicating a value for $D(CO)$ in the neighbourhood of 8·8 eV. This gives better support to the spectroscopic value 9·144 eV than to the electron-impact value 9·6 eV or any higher figure; that is to say, it indicates that the heat of atomization of carbon is 125·0 kcal rather than 136 kcal or more. These conclusions confirm those derived from independent data elsewhere[2]. It is not however claimed that these deductions based on extrapolation procedures are sufficiently conclusive to exclude the electron-impact figure for $D(CO)$. Apart from the approximate nature of the method, it has not yet been tried out in a sufficient number of cases for judgment to be passed concerning its general reliability. For the moment, attention should be paid to its indicative value.

[1] L. PAULING and W. F. SHEEHAN, *loc. cit.*

[2] L. H. LONG, Proc. Roy. Soc. A *198*, 62 (1949).

[3] L. H. LONG, Research, London *3*, 291 (1950).

[4] G. HERZBERG and J. G. PHILLIPS, Astrophys. J. *108*, 163 (1948).

The case of CN is also very instructive. It has long been known that the excited $A\ ^2\Pi$ state extrapolates to a convergence limit which is appreciably below that of the ground state, a rather unusual state of affairs which has evoked comment from other investigators. The extrapolated curves therefore cross (see fig. 2). This is however exactly what would be expected if the carbon in the ground $X\ ^2\Sigma$ state is tetravalent, but divalent in the upper state. This interpretation is supported by the interatomic distances and chemical behaviour of CN[1]. The ground state extrapolates to 9·85 eV. Deducting 5·11 eV for the dissociation energy of CN[2] and 1·84 eV for the valence energy of nitrogen[3] yields 2·90 eV or 67 kcal for the valence energy of tetravalent carbon, in excellent agreement with the previous estimates.

The estimates in this section, like those in the last, are of course only approximate. The discrepancy between the respective figures, namely 66, 57, 65, and 67 kcal, can be readily explained when it is remembered that the latter contain uncertainties in intrinsic bond energies derived by the extrapolation method, and that values which are not highly accurate have been employed for the energies of the divalent states of carbon and oxygen. Transferring valence energies from molecule to molecule in general involves the neglect of energy differences arising through different mixing of the electron orbitals. Such differences are probably small in comparison with the energies involved in transitions involving definite electron jumps, but it is doubtful if they are quite negligible. For example, the value adopted for the divalent state of carbon was derived from data for the molecules CH and C_2. The bonding is in neither case identical with that in CO and CN, and the possibility that the internal energy of the carbon differs in the four cases by perhaps several tenths of an electron-volt cannot be excluded. These are some of the difficulties which will have to be faced in a perfect treatment.

5. *Concluding Remarks*

The foregoing discussion illustrates the importance of valence states when considered in relation to bond properties and the energetic aspect of molecular structure in general. The various lines of reasoning which have been brought forward for the example of tetravalent carbon agree in pointing to an energy level for the valence state which is some 60–70 kcal above the ground state, and it would not be possible to select a value far outside these limits without coming into conflict with experimental evidence. From the experimental side, the accuracy of the derivation of valence states from dissociation energies will improve with increasing knowledge regarding the energies of reorganization of molecular fragments. From the theoretical side, brave attempts have already been made by a number of physicists to grapple with this difficult problem, and it is to be hoped that a reliable method for calculating valence energies will eventually become available.

It is to be noted that dissociation energies can be employed to estimate heats of atomization of elements only with a knowledge concerning the relevant valence states. Failure to recognize this has led to erroneous conclusions in the past. For example, it has on more than one occasion been suggested in print that the value of $D(CH_3-H)$ supports the high value 170 kcal for the heat of atomization of graphite, which value is incompatible with other data. Similar arguments applied to experimental values for $D(HO-H)$ and $D(NH_2-H)$ would indicate heats of atomization for oxygen and nitrogen which are in excess of the true values, since the valence energies of these elements are considerable.

In the case of carbon, the energy required to promote an *s* electron for the purpose of chemical bonding is seen to be of a similar order to, but less than, the promotional energy of an *s* electron in the free atom. If reasonable values are to be assumed for intrinsic bond energies, the same seems to hold for other like cases, as for the instance of N^+ in the ammonium ion. Further examples are provided by the elements in groups II, III, and IV which stand four, five or six places before a rare gas. Thermochemical data for the volatile alkyls of a number of these elements[1] indicate that the promotional energy of an *s* electron for the combined atom lies in each case between 60 and 100% of that for the free atom.

Zusammenfassung

Die Theorie von Valenzzuständen wird im Zusammenhang mit wahren oder «intrinsischen» (als verschieden von thermochemischen) Bindungsenergien diskutiert.

Mit den augenblicklich zur Verfügung stehenden Kenntnissen können nur annähernde Schätzungen der Energien der Valenzzustände gemacht werden. Dies ist für das Beispiel von vierwertigem Kohlenstoff mit einer Anzahl von unabhängigen Methoden unternommen worden. Der angedeutete Wert ist etwa 60–70 kcal höher als der Grundzustand. Da der Valenzzustand in Beziehung mit der Sublimationswärme des Kohlenstoffs steht, liefert er Belege bezüglich des letzteren.

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[1] For more details, see L. H. LONG, Research, London, *3*, 291 (1950).

[2] L. H. LONG, *loc. cit.*

[3] L. PAULING and W. F. SHEEHAN, *loc. cit.*

[1] L. H. LONG and R. G. W. NORRISH, Phil. Trans. Roy. Soc. A, *241*, 587 (1949).

Nota

Archives of Biochemistry and Biophysics)

In view of the ever-increasing use of physical methods in problems of biochemistry—especially in borderline fields, Academic Press announces the intended widening of the scope of its journal, *Archives of Biochemistry*.—In addition to established biochemical topics, the Editors will consider manuscripts in the fields of virus research, radiation effects on living matter, macromolecular biology and chemistry, studies of the application of radioactive indicators, and physics of biological systems.

Beginning with Volume XXXI, Number 1, March 1951, the title of *Archives of Biochemistry* will be changed to *Archives of Biochemistry and Biophysics* to indicate more accurately the new scope of the journal. The Editorial Board has also been enlarged; Drs. E. NEWTON HARVEY, E. C. POLLARD, and R. W. G. WYCKOFF have accepted an invitation to serve.