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.

[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.

[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.