QUARTERLY REVIEWS

COMMENTS ON THE THERMOCHEMISTRY OF THE ELEMENTS OF GROUPS IVB AND IV

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Section I

THE heat of any chemical reaction is the algebraic sum of the heats of formation Q_f of the compounds concerned from their elements in conventionally chosen standard states. Heats of formation of gaseous compounds are not complicated by interactions between molecules, and such heats of formation Q_f^a related to free atoms in the gas phase as standard states are simpler in theory than the conventional Q_f values. The problem of understanding thermochemistry starts therefore with Q_f^a values.

If a molecule XY_n has n bonds in it, all the same, then we may define a bond energy $B(X\text{–}Y)$ by

$$B(X\text{–}Y) \equiv \frac{1}{n} Q_f^a(XY_n) \quad . \quad . \quad . \quad . \quad (1)$$

It is found that such bond energies are often approximately the same in several molecules. For example, the heats of the several steps (where $X = Cl$, Br, or I):

$$\begin{array}{llllll} CH_4 & + X & \longrightarrow & CH_3X & + H \\ CH_3X & + X & \longrightarrow & CH_2X_2 & + H \\ CH_2X_2 & + X & \longrightarrow & CHX_3 & + H \\ CHX_3 & + X & \longrightarrow & CX_4 & + H \end{array}$$

are approximately equal, so that one can consider each process as the loss of a C–H bond energy and the gain of a C–X bond energy.[1]

The history of this bond-energy concept is divided fairly clearly into three main periods. In the first,[2] the object was to investigate the constancy of bond energies as between different molecules.[3] In the second period, attention became directed to the anomalies: this development is mainly due to Pauling [4] who, by use of the quantum-mechanical concept of "resonance" explained many such anomalies and the numerical values

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[1] Baughan, *Nature*, 1941, **147**, 542.
[2] Fajans, *Ber.*, 1920, **53**, 643; 1922, **55**, 2836; see also Grimm, Sidgwick, and others.
[3] Cf. Sidgwick, "The Covalent Link in Chemistry", Cornell Univ. Press, 1934.
[4] "The Covalent Link in Chemistry", Cornell Univ. Press, 1940.

of many bond energies themselves. The great successes of Pauling's method has led naturally enough to the third, modern development of the question.

Here the real issue is to make the concept of bond energies do two things at once. Any refinements of the bond-energy concept must retain the original ability to predict the Q_f values of molecules ; the problem now is to use bond energies for other purposes as well, *viz.*, to correlate bond energies with, *e.g.*, molecular ionisation potentials,[5] or bond distances and force constants,[6, 7] or dipole moments,[8, 9] or with the dissociation energies of *individual* links to give free radicals : $\frac{1}{4}Q_f^a(CH_4)$, for example, with the heat of reaction $CH_4 \longrightarrow CH_3 + H$. Evidently, any such single-step dissociation energy can be given as the difference between the Q_f^a of a molecule and those of the free radicals or atoms into which it dissociates ; the problem of dissociation energies can, to begin with, be reduced to that of : What is the relation between the bond energies in cases where one of the atoms is in a different valency ?

To this problem quantum mechanics at present gives no simple quantitative answer.[10] It is, however, a problem of great practical importance. The calculation of the heats of formation of stable well-known molecular species is a problem in which, as experimental chemistry so long preceded quantum physics, theory mainly reduces to order what is already known. Considering, however, free radicals in chain reactions, surface hydrides in catalytic processes,[11] compounds unknown in " bottle " quantities at room temperature but of major importance in metallurgical and combustion reactions, we see that many problems still involve unknown heats of formation of compounds of " unusual " valency ; and, in the absence of any clear guide from theory, we must try to see what empirical general rules can be stated about the dependence of bond energies on valency.

Such a programme accentuates the great uncertainty in the heats of formation of so many elements as free gaseous atoms from their conventional standard states (" heats of atomisation "). Yet on the one hand, the earlier investigations [3] assumed many heats of atomisation which are either still the subject of controversy (*e.g.*, carbon, nitrogen) or have since been shown to be wrong (*e.g.*, oxygen, fluorine) ; on the other hand, modern investigators claim to *deduce* heats of atomisation from bond energies. Evidently, for some applications of bond energies the heats of atomisation cancel out, but for others they do not. If one confines attention to Q_f values for molecules, conversion of these into Q_f^a values leaves the bond energies constant as between different molecules *as long as the valency may be considered constant.* An error of x in the heat of atomisation of carbon, for example, implies an error of $\frac{1}{4}x$ in *all* single bonds to carbon, $\frac{1}{2}x$ in *all* C–C bonds, etc. It would therefore have been possible to discuss additivity relations in heats of

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[5] Walsh, *Trans. Faraday Soc.*, 1946, **42,** 56 ; 1947, **43,** 60, 158.

[6] Fox and Martin, *J.*, 1938, 2106.

[7] Baughan, *Trans. Faraday Soc.*, 1948, **44,** 845.

[8] Linnett, *ibid.*, 1940, **36,** 1123.

[9] Cottrell and Sutton, *Quart. Reviews*, 1948, **2,** 260 ; see also ref. (4).

[10] Coulson, *Discuss. Faraday Soc.*, 1947, **2,** 9.

[11] Cf. Eley, *ibid.*, 1950, **8,** 34.

formation without bringing in heats of atomisation at all, and this was in fact sometimes done.[12] For example, the " resonance energy " of the benzene molecule could either be obtained from bond energies or directly by comparing the heat of hydrogenation of benzene with those of ethylenic hydrocarbons ; the two methods agree to within the considerable uncertainties imposed by neglect of the vibrational and rotational energies involved.[13]

When we come to the numerical values of bond energies, the position becomes more subtle. The empirical issue involved in Pauling's use of " ionic-covalent resonance energies " is to compare the single bond energy B(X–Y) with the mean of B(X–X) and B(Y–Y). Provided that we consider the arithmetic mean, and that the heats of atomisation A_x, A_y, of X and Y are simply related to the single-bond energies, then A_x, A_y may vanish. This condition may be justified for hydrogen, the halogens, and the elements carbon, silicon, germanium, and tin, but it is certainly not legitimate for nitrogen, for example.

Further, when we come to the problem of dissociation energies, heats of atomisation cannot be neglected even in the first approximation. It is an obvious first simplification to suppose that the dissociation energy of $CH_4 \longrightarrow CH_3 + H$ should be simply equal to the bond energy in CH_4, though this view cannot be justified theoretically, or to suppose that they would be equal if one referred the bond energies to a spectroscopically excited state of carbon [14]—although the *tetrahedral* symmetry of CH_4 argues for hybridisation ; but one cannot begin to check either hypothesis unless one can put a number to the bond energy of CH_4 ; the full $\frac{1}{4}x$ uncertainty is involved.

It is therefore of crucial importance to improve our knowledge of heats of formation of atoms and radicals and more experiments are needed. But one can often improve the heats of atomisation derived from existing data on equilibrium constants, and this has not always been done. High-temperature equilibrium data measure at T a free-energy change ΔG°_T. From this we can derive ΔH°_T (and hence ΔH°_0 the value at 0° K) *either* from the variation of ΔG°_T with T (plot $\log K$ against $1/T$ and find the slope ; second-law method), *or* by computing, from specific-heat data and the quantum-statistical theory of entropy, ΔH°_0 from each single value of ΔG°_T (third-law method). It is not universally realised that the latter method is the better. First, it reduces a problem in two variables to a problem in one variable. Secondly, correct third-law values of ΔH°_0 must agree with the correct second-law values ; we have therefore a check on the data. Thirdly, high-temperature equilibria are not easy to measure and the measurements often involve systematic errors. The second-law method depends on differences, usually small, in ΔG°_T, the third-law method on its absolute value. Evidently the latter is less sensitive to systematic errors.

So far we have mentioned calorimetric and equilibrium-constant data.

[12] Cf. Kharasch, *Bull. Bur. Stand. J. Res.*, 1929, **2**, 359.
[13] See Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767.
[14] Long and Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337.

Other methods are also available. In a polyatomic molecule, CH_4 for example, the first-stage dissociation energy ($CH_4 \longrightarrow CH_3 + H - D_4$ kcal.) can often, and later stages occasionally, be obtained from kinetic measurements,[15] particularly from low-pressure pyrolysis reactions, or from mass-spectrometer experiments where electron bombardment produces both ionisation and bond-fission.[16] The dissociation energy of the last stage ($CH \longrightarrow C + H - D_1$ kcal.) is the quantity usually known as D_0^0 by spectroscopists—the dissociation energy of a diatomic molecule into atoms in their ground states. And from Hess's law the bond energy (as defined in equation 1) is related to these dissociation energies D by

$$\sum_n D_n = nB \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It may be pointed out that errors in the spectroscopic determination of dissociation energies are of two kinds : (*a*) errors of extrapolation from the highest measured state of vibrational excitation to the limit of complete dissociation ; such errors are *continuous* (in the mathematical sense) :

(*b*) errors of identification. A dissociation energy of a molecule may be *exactly* known, but the products of dissociation unknown—one or both of the atoms may be in excited states. But the possible excitations of most common atoms are well known, and there are theoretical rules which limit the possible atomic states into which a given diatomic molecular state can dissociate. Hence the errors of this second kind are errors of choice between a *discrete* set of a few possible values (such are the notorious cases of CO and N_2 [17]), so that a rough thermochemical estimate may rule out all identification possibilities but one, which can then, in its turn, make the thermochemical estimate much more precise. The use of third-law methods again increases the precision of this argument.

Besides giving many such dissociation energies (and hence many heats of atomisation) molecular spectroscopy also provides the basis for another attack on the problem. For a diatomic molecule XY one can obtain the fundamental vibrational frequency (and hence the force constant) and often the interatomic distance as well, though this is often impracticable because of isotopic complexity or complexity of rotational levels.[17, 18] Equally for molecules XY_n the X–Y distances can be obtained from electron and *X*-ray diffraction experiments (occasionally by spectroscopic methods),[19] and the force constants can be obtained from the vibrational frequencies, though unfortunately the results depend on the particular form of the fields of force assumed.[20]

We have therefore the material for a new way of searching for an interpretation. In principle there are two extreme types of variation in a series

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[15] For reviews see Szwarc, *Chem. Reviews*, 1950, **47**, 75 ; *Quart. Reviews*, 1951, **5**, 22.

[16] Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35.

[17] See Gaydon, " Dissociation Energies and Spectra of Diatomic Molecules ", Chapman & Hall, London, 1947.

[18] Herzberg, " Spectra of Diatomic Molecules ", Van Nostrand Co., New York, 1950 ; Table 39 in this book gives a very complete summary of data.

[19] For a summary of data see Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

[20] Linnett, *Quart. Reviews*, 1947, **1**, 73.

of molecules. In the one, the energy, force constant, and distance all vary together, the first two increasing as the distance decreases ; the difference in energy is therefore partly, if not entirely, due to factors which affect the equilibrium properties of the bond. It appears probable that the C–C, C=C, C≡C and the conjugated bonds of organic chemistry are an example of this type of variation, since simple empirical equations account for the phenomena.[6, 7] Such a variation we may call an " equilibrium variation " in bond energy. The other logical extreme case is where the *equilibrium* properties of an X–Y bond do not vary, although the bond energies vary considerably. Here the difference in energy must be due to factors which do *not* affect the bond in the molecule, but affect only the products into which it dissociates. This kind of variation we may call " separation variation " in bond energy. This empirical distinction may serve as a check on theoretical interpretation ; Long and Norrish's " reorganisation energy " concept,[14] for example, clearly implies some " separation variation ".

But the application of these ideas to radicals XY and corresponding molecules XY_n involves a further complication, in that the repulsion forces between " non-bonded " Y atoms, the chlorines in CCl_4 for example, must be considered. Such computations have been applied in the past to the calculation of force constants, but the same principles can simply be extended to other equilibrium properties of the X–Y bond.

This introductory discussion leads to a general programme of investigation of bond energies in compounds of " unusual " valency, and to suggestion of *methods* : (*a*) To discuss bond energies as far as possible without introducing heats of atomisation at all. (*b*) In cases where heats of formation of " unusual " molecules depend on high-temperature equilibria, to use third-law rather than second-law methods to deduce heats of reaction. (*c*) To compare, as far as possible, the results of kinetic, spectroscopic, and thermochemical experiments on bond properties *together*, with due regard to the effects of " non-bonding " regulations.

The present Review attempts such a programme, inevitably still incomplete, for the peculiarly suitable group of elements carbon, silicon, germanium, tin, lead ; other elements are considered only in so far as they illuminate the problems arising in this Group.

Section II

As already pointed out, conclusions drawn from the heats of formation of *series* of molecules do not depend on heats of atomisation. We shall therefore not discuss such applications, successful though they are.[21] There are, however, points worth reconsidering about " ionic-covalent resonance ", and these are the subject of the present Section.

This " semi-empirical " quantum idea of Pauling's is invoked to explain bond energies themselves. If B(X–Y), B(X–X), B(Y–Y) are the bond energies (equation 1) of single bonds between the elements concerned, then it is generally found that B(X–Y) is greater than the mean of B(X–X) and

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[21] Cf. Wheland, " The Theory of Resonance and its Application to Organic Chemistry ", Chapman & Hall, London, 1944 ; John Wiley, New York.

B(Y–Y). Considering the arithmetic mean, Pauling defines an " ionic-covalent resonance energy " R_{xy} by the equation

$$B(\mathrm{X{-}Y}) = \tfrac{1}{2}[B(\mathrm{X{-}X}) + B(\mathrm{Y{-}Y})] + R_{xy} \qquad . \quad . \quad (3)$$

Admittedly, the geometric mean gives a better correlation, but a geometric mean of bond energies implies their absolute values, and hence requires heats of atomisation.

The arithmetic mean, however, in some special cases does *not* require heats of atomisation. It is easy to prove that if the standard states of hydrogen and the halogens be taken as diatomic gases, with dissociation energy equal to their single-bond energy, and that if the standard states of C, Si, Ge, Sn be taken as the quadrivalent diamond-type crystals (grey tin, not the metallic form) with each atom the centre of four single bonds, then for the halogen hydrides, the interhalogen compounds (XY), and the tetrahedal Group IV halides XY_n

$$Q_f^*(\mathrm{XY}_n) = n\, R_{xy} \qquad . \quad . \quad . \quad . \quad (4)$$

where the asterisk on Q_f^* implies this somewhat unusual choice of thermochemical standard states.

For these particular sets of compounds the evaluation of R_{xy} is therefore independent of any knowledge of heats of atomisation, provided only (*a*) that the standard states may be regarded as singly bound in the valency sense, and (*b*) that the arithmetic-mean approximation is adequate. This point is indeed made by Pauling[4] but does not, perhaps, appear to be generally realised. It may be emphasised that no such simplification is possible for such important elements as O, N, P.

In Table 1 therefore are given the heats of formation of these molecules in the ordinary convention, and then Q_f^* in the modified convention, and hence the " ionic-resonance energy " R_{xy} defined in equation (3).

TABLE 1[21a]

(All compounds gaseous)

	Q_f	Q_f^*	R_{xy}	$x_x - x_y$		Q_f	Q_f^*	R_{xy}	$\lvert x_x - x_y \rvert$
HF	64·0	$= Q_f$	64·0	1·9	SiH_4	8·7	$= Q_f$	2·2	0·3
HCl	22·1	$= Q_f$	22·1	0·9	SiF_4	360·1	$= Q_f$	90·0	2·2
HBr	8·7	12·5	12·5	0·7	$SiCl_4$	142·5	$= Q_f$	35·6	1·2
HI	− 5·9	+ 1·5	1·5	0·4	$SiBr_4$	83·7	99·0	24·8	1·0
FCl	25·7	$= Q_f$	25·7	1·0	SiI_4	16·1	45·9	11·5	0·7
ICl	− 3·5	+ 4·0	4·0	0·5	$GeCl_4$	216	$= Q_f$	54·0	1·2
BrCl	− 3·1	+ 0·8	0·8	0·2	$GeBr_4$	—	83·3	20·8	1·1
CH_4	18·2	$= Q_f$	4·6	0·4	GeI_4	—	42·0	10·5	0·7
CF_4	231	$= Q_f$	57·8	1·5	$SnCl_4$	118·4	119·0	29·8	1·3
CCl_4	25·9	$= Q_f$	6·5	0·5	$SnBr_4$	79·7	94·2	23·5	1·1
CBr_4	− 12	+ 3·5	0·8	0·3					

[21a] All Q_f values are from Bichowsky and Rossini, " Thermochemistry of Chemical Substances ", Reinhold, New York, 1937, *except* : CF_4 from von Wartenberg, *Nachr. Akad. Wiss. Göttingen* (Mat. Phys. Abt.), 1946, p. 57 ; $GeBr_4$, GeI_4 from Evans and Richards, *J.*, 1952, 1293.

Pauling [4] points out a further remarkable correlation that

$$R_{xy} = \text{const.}\ | x_x - x_y |^2 \quad . \quad . \quad . \quad . \qquad (6)$$

where x_x and x_y are empirical coefficients (whose scale is evidently arbitrary), characteristic only of the atoms X and Y and independent of their partners in the bond. These coefficients are called " thermal electronegativities ". The last column in Table 1 gives his values of $| x_x - x_y |$ and in Fig. 1 we plot $\sqrt{R_{xy}}$ against $| x_x - x_y |$ for these compounds ; it can be seen that a straight line passes well through these points. For $| x_x - x_y | = 1$, $\sqrt{R_{xy}} = 4{\cdot}7$, or $R_{xy} = 22$, in excellent agreement with Pauling's value 23 recommended on the basis of many data, some of which are, however, less certain.

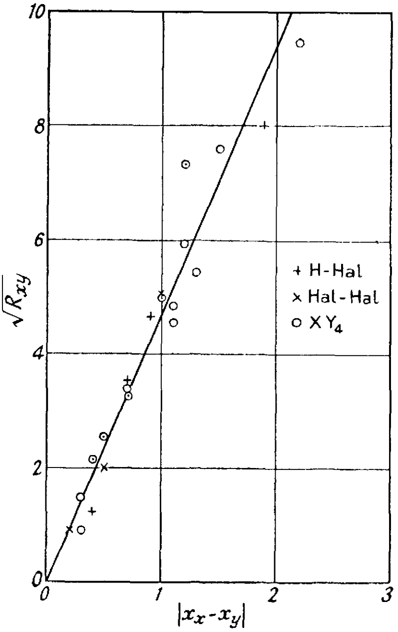

FIG. 1

On this specially restricted sample of 21 R_{xy} values depending on 9 elements the empirical rule fits well. As a general rule it has been criticised by Burawoy,[22] who emphasises two matters. (*a*) A few cases appear to show *negative* values of R_{xy}. Some of these anomalies disappear if one chooses a geometric mean ; others remain. It may, however, prove significant that most of the elements concerned in these anomalies are those whose heats of atomisation are peculiarly difficult to measure—the elements of Groups V and VB, VI and VIB of the Periodic Table—and cannot be simply eliminated ; the results for oxygen, whose heat of atomisation is accurately known, are satisfactory. (*b*) The correlation between R_{xy} and thermal electronegativity is particularly inexact in the case of bonds involving hydrogen, an important deduction for which Burawoy's factual evidence, though partly unsatisfactory, is still conclusive.

So far the thermal electronegativities are purely empirical coefficients, whose significance depends on whether from N such coefficients and N B(X–X) values we can, in fact, account for the single-bond energies between N elements [$\frac{1}{2}N(N-1)$ in number]. That we are really dealing with an *electrical* property of a bond is made very probable by the rough correlation of x with the XY bond dipole moment, and the proportionality between the thermal electronegativity of an atom and the sum of its ionisation potential I and electron affinity E.[23] Here the empirical correlation actually

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[22] *Trans. Faraday Soc.*, 1943, **39**, 79.

[23] Mulliken, *J. Chem. Phys.*, 1934, **2**, 782 ; 1935, **3**, 573.

given in Pauling's book [4] refers only to " the univalent elements, hydrogen, the halogens, the alkali metals, for which the treatment is straightforward ".

The subsequent neglect of this very striking relationship arises from two causes. First, it appears to be generally believed that, although ionisation potentials are well known, yet not enough is known about electron affinities in the middle of the Periodic Table for the sum $(I + E)$ to be evaluated. Secondly, Mulliken's discussion [23] points out that the I and E values should really refer to the " valence states " of the atoms, *not* to their spectroscopic ground states. This conclusion is inescapable.

However, the actual facts are surprisingly simple. Electron affinities *can* be roughly estimated for ground-state atoms, and since I is much larger than E, the sum $I + E$ can be estimated about as precisely as the thermal electronegativity itself; the ratio E/I is highest for the halogens where it varies from 0·23 for fluorine to 0·33 for iodine, for hydrogen it is only 0·05, and for carbon about 0·10; and the sum $I + E$ *is* very closely proportional to the " thermal electronegativity ", *even for multivalent elements.*

TABLE 2

Element		H	Li	Be	B	C	N	O	F
I . .	. .	13·59	5·40	9·32	8·28	11·27	14·55	13·62	17·43
E . .	. .	0·72	0·4	−0·6	0·1	1·1	0·1	2·2	4·1
$I + E$.	. .	14·31	5·8	8·7	8·4	12·4	14·6	15·8	21·5
x(obs.) .	. .	2·1	1·0	1·5	2·0	2·5	3·0	3·5	4·0
x(calc.) .	. .	2·8	1·1	1·7	1·6	2·4	3·0	3·1	4·1
Element	Na	Mg	Al	Si	P	S	Cl	Br	I
I . .	5·14	7·64	5·97	8·15	10·9	10·36	12·90	11·76	10·44
E . .	0·1	−0·9	0	0·6	0·2	2·0	3·73	3·52	3·21
$I + E$.	5·2	6·7	6·0	8·8	11·1	12·4	14·6	15·3	11·6
x(obs.)	0·9	1·2	1·5	1·8	2·1	2·5	3·0	2·8	2·4
x(calc.)	1·0	1·3	1·2	1·7	2·1	2·4	2·8	3·0	2·6

For the halogens, accurate (± 1 or 2%) values of E can be obtained from the lattice-energies of ionic crystals and the Born–Haber cycle; for a few other elements values are obtainable from electron-bombardment experiments. For most elements we must employ another "semi-empirical" argument. In the ionisation potentials of a series of atoms and ions like B, C^+, N^{++}, O^{+++}, F^{++++}, we are concerned with the same number of electrons but with changes by unity in the nuclear charge; hence, extrapolation back would give the ionisation potential of Be^-, which is, with due regard to sign, the electron affinity.

How should this extrapolation be made? For atoms and ions with *two* external electrons, the ionisation potentials, calculated by a variational method, agree with experiment to within a few thousandths of a volt. The results are expressible as a series in direct and inverse powers of the atomic number Z, of which all but the first two or three terms are very small.[24] Glockler,[25] expressing such series of isoelectronic ionisation potentials for more complex cases as similar series in Z, but with different coefficients, obtained electron affinities for the elements in the two short periods, agreeing to within about 0·4 volt with the Born–Haber values for the halogens, and supported in many cases by computation from Slater eigenfunctions.[26] In Table 2 are shown, therefore, the values of I and E for those elements for which such rough estimates of E have been made, and the thermal electronegativities x (from Table II—3 in Pauling's book [4]). The I and E values [4] are in electron-volts (1 e.v. per atom = 23·06 kcal. per g.-atom).

It can be seen from Fig. 2, where these points are plotted, that the graph of $I + E$ against x is a good straight line passing through the origin —the point for H being badly off the line, and the points for B, Al, and O significantly off it. The hydrogen anomaly is striking in view of Burawoy's criticisms just referred to. The equation to this line is

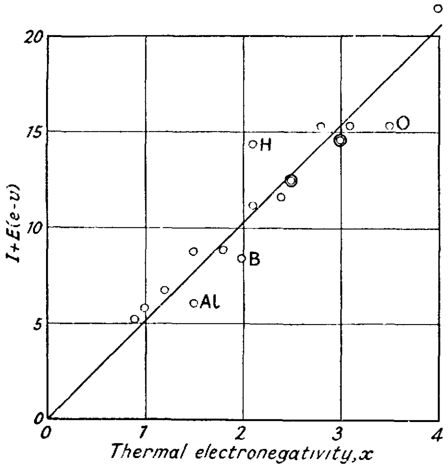

FIG. 2

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\left.\begin{aligned}
x &= 0{\cdot}193\,(I + E) \\
\text{or} \qquad (I + E) &= 5{\cdot}15x\,(I + E \text{ in volts}) \\
&= 119x\ (I + E \text{ in kcal./g.-atom})
\end{aligned}\right\} \quad . \quad . \quad . \quad (7)
$$

and this last coefficient may be directly compared with Pauling's 130 on the smaller sample. In the last line of Table 2 are given the values of the thermal electronegativity calculated from this equation.

Again we have a general relation with individual exceptions. Provided, however, the empirical relation holds, one conclusion may be drawn. Mulliken's arguments prove conclusively that the $(I + E)$ value which should be considered as a measure of electronegativity is that related to the valency

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[24] Hylleraas, *Z. Physik*, 1930, **65**, 209.

[25] *Phys. Rev.*, 1934, **38**, 111.

[26] Hellmann and Mamotenko, *Acta Physiochim. U.R.S.S.*, 1938, **7**, 1.

state. In fact, the $(I + E)$ for the ground state is, as we have seen, proportional to Pauling's thermal electronegativity for the *usual valency state* (carbon quadrivalent, for example). The conclusion may therefore be provisionally drawn that *the thermal electronegativity of an atom in different valency states depends but little on its particular valency state.*[23]

This principle, if true, would greatly simplify our problem. For it would enable, for example, the bond energy in a compound AX_2 to be estimated from that in AY_2 if one knew the bond energies in AX_4 and AY_4. It would permit discussion of sets of bond energies for different valencies in terms of the one numerical parameter, the " excitation energy of the valency state ". And once more, if we may accept the arithmetic-mean approximation, the verification of this hypothesis need not always require a knowledge of the heats of atomisation.

There is at any rate one case where we have fairly precise data for the bond energies of molecules XY and XY_2 : the mono- and di-halides of mercury.[27, 28] The heats of formation of $HgHal_2$ are well known (cf. Bichowsky and Rossini [21a]), the heat of atomisation of Hg from its vapour-pressure curve which has been well established, and the dissociation energies D_0^0 of HgHal from spectroscopic data.[27, 29] If we call ${}_2B$ the bond energy in the $HgHal_2$ molecule, and ${}_1B$ that in the diatomic radical $(=D_0^0$ by definition), then we may draw up the following Table :

	${}_1B$	${}_2B$	${}_2B - {}_1B$
$Hg—Cl_2$	24	52·2	28·2
$Hg—Br_2$	16·4	44·0	27·6
$Hg—I_2$	9	34·5	25·5

The rough constancy of ${}_2B - {}_1B$ is encouraging (the ${}_1B$ values refer to 0° K, and the ${}_2B$ values to 291° K) and a similar test on the tri- and penta-halides of phosphorus and the di- and tetra-halides of tin also shows rough agreement.[28]

It is instructive to compare this hypothesis with a proposal for simplifying bond energies put forward by Dewar [30] who states that " it is possible to modify the bond-energy table so that the values for the bond energy and the dissociation energy " (which he there calls bond strength) " of any bond are equal if we take the heat of formation to refer to formation from atoms in arbitrary energy states " and that " such energy states should be regarded as arbitrary parameters the value of which should be so chosen that the bond energies of carbon bonds should be equal to their breaking-energy (dissociation energy)."

It is, as we have already pointed out, legitimate to reckon Q_f values for molecules from *any* arbitrary zero, provided one restricts discussion to whether bond energies are constant in a series of molecules of the same

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[27] Cf. Wehrli and Milazzo, *Helv. Chim. Acta*, 1939, **26**, 1025.

[28] Skinner, *Trans. Faraday Soc.*, 1949, **45**, 20.

[29] Wieland in " Les Spectres Moleculaires ", CNRS, Paris, 1947.

[30] " Electronic Theory of Organic Chemistry ", O.U.P., 1949, pp. 32, 33, 37.

valency. But a dissociation energy involves a difference in bond energy between two molecules of *different* valency (*e.g.*, CH_3 and CH_4). If, for example, one chooses the zero to give $D(CH_3{-}H)$ equal to $B'(CH_4)$, the bond energy of CH_4 reckoned from this zero, why should the *same* choice of zero be valid for CCl_4 and CCl_3 ? Clearly it will *not* be, unless the R_{xy} terms are the same in CCl_3 as in CCl_4. Reasons have just been given for supposing that this may be true, but Dewar's argument rests on a confusion between experimental fact and arbitrary convention.

Another application of thermal electronegativities is due to Schomaker and Stevenson,[31] according to whom an X–Y bond should be *shorter* than corresponds to the mean of lengths of the X–X and Y–Y bonds by an amount directly proportional to $|x_x - x_y|$. Once more the compounds of the types considered in Table 1 are particularly suitable for investigation, for the single-bond distances in H_2, F_2, Cl_2, Br_2, I_2, and in the halogen hydrides are well known from spectroscopic data, and in carbon (diamond), silicon, germanium, and grey, tetrahedral, tin from accurate *X*-ray work.[32] We may take from these values the following single-bond distances : H_2 0·742, F_2 1·435, Cl_2 1·988, Br_2 2·284, I_2 2·667, C—C 1·541, Si—Si 2·346, Ge—Ge 2·446, Sn—Sn 2·811 Å. In Table 3 are given therefore (*a*) the observed distances,[18, 19] (*b*) the internuclear distance predicted as a mean ("additivity of covalent radii"), (*c*) the contraction of the bond (additive minus observed), (*d*) the difference $|\Delta x|$ in electronegativity according to Pauling. The contractions are plotted against $|\Delta x|$ in Fig. 3.

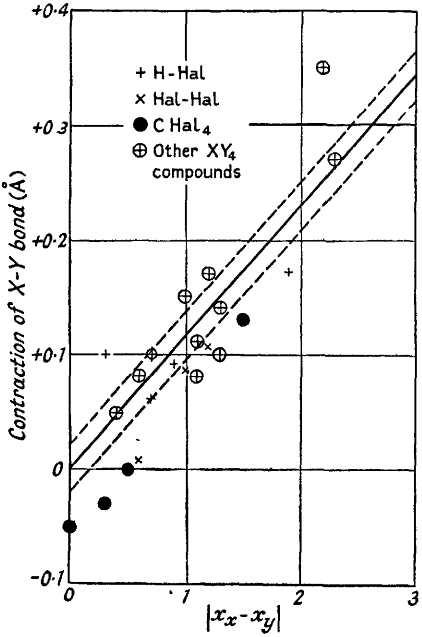

FIG. 3

If Δr is the contraction in Å then

$$\Delta r = 0{\cdot}11_4\,|x_x - x_y| \quad . \quad . \quad . \quad . \quad (8)$$

with a probable error in the slope of about ± 20% (cf. Schomaker and Stevenson's slope 0·09) ; the two companion dotted lines correspond to ± 0·02 Å. It may be seen that 16 of the 23 points plotted lie round this

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[31] *J. Amer. Chem. Soc.*, 1941, **63,** 37.

[32] For diamond, see Landolt–Bornstein's " Tabellen " ; for silicon, Jette and Foote, *J. Chem. Phys.*, 1935, **3,** 615 ; for germanium, Nitka, *Physikal. Z.*, 1937, **38,** 896 ; for tin, Brownlee, *Nature*, 1950, **166,** 482.

TABLE 3

	$d_{\text{obs.}}$	d_{additive}	Contr.	$\lvert \Delta x \rvert$		$d_{\text{obs.}}$	d_{additive}	Contr.	$\lvert \Delta x \rvert$
HF	0·917	1·089	0·172	1·9	$SiCl_4$	2·02	2·167	0·15	1·2
HCl	1·275	1·365	0·090	0·9	$SiBr_4$	2·15	2·315	0·17	1·0
HBr	1·414	1·513	0·099	0·7	SiI_4	2·43	2·506	0·08	0·6
HI	1·604	1·704	0·100	0·3	GeF_4	1·67	1·941	0·27	2·3
BrF	1·756	1·860	0·104	1·2	$GeCl_4$	2·08	2·217	0·14	1·3
ClF	1·628	1·712	0·084	1·0	$GeBr_4$	2·29	2·365	0·08	1·1
ICl	2·321	2·328	0·007	0·6	GeI_4	2·50	2·556	0·06	0·7
CF_4	1·36	1·488	0·13	1·5	$SnCl_4$	2·30	2·400	0·10	1·3
CCl_4	1·76	1·764	±0	0·5	$SnBr_4$	2·44	2·548	0·11	1·1
CBr_4	1·94	1·913	−0·03	0·3	SnI_4	2·64	2·739	0·10	0·7
CI_4	2·15	2·104	−0·05	0·0	CH_4	1·093	1·142	0·049	0·4
SiF_4	1·54	1·890	0·35	2·2					

line with deviations which are in many cases of about the magnitude to be expected. In other cases the deviations are beyond experimental error, so it is clear that the rule is only a good first approximation, but the points badly off the line merit special consideration. The scatter of the points at very high Δx may not mean anything ; there is no theoretical reason for a strictly linear relationship (it is, indeed, rather unlikely) and it would be easy to choose some other functional form which would represent the lower points equally well and yet curve upwards. Two outstanding discrepancies are left : (*a*) that the point for HI is too high, and that for ICl too low (curiously enough, the carbon–iodine bond also has an anomalously low resonance energy R_{xy}) ; (*b*) that *all* the contractions for the carbon halides are too small, being actually *negative* for CCl_4, CBr_4, and CI_4. These bonds are, from Fig. 3, all about 0·06 Å too long. We shall show later that this abnormal length of carbon–halogen bonds may be predicted from the " non-bonding " repulsions.

The discussion so far shows the value of the empirical concept of electronegativity ; the selected facts of this Section leave little doubt as to its general applicability, or, on the other hand, as to there being individual discrepancies. Recently, there has been a discussion of these ideas before the Royal Society.[33] From the theoretical side (Cottrell and Sutton, Coulson, and others) it is difficult to see why they should work so well, yet Warhurst has applied them even to the second-order effect involved in the changes of molecular vibration frequencies of given solutes in different solvents, and Walsh has pointed out some remarkable correlations between electronegativities and bond vibration frequencies. These are the more remarkable in that vibration frequencies themselves appear subject to empirical regularities of very simple form.[34] One may venture the opinion that the search for empirical regularities will yield yet further results.

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[33] *Proc. Roy. Soc.*, 1951, *A*, **207,** 1—74.

[34] Guggenheimer, *Proc. Phys. Soc.*, 1946, **58,** 456 ; *Discuss. Faraday Soc.*, 1950, **9** ; Baughan, *Trans. Faraday Soc.*, 1952, **48,** 121.

Section III

In this Section we are concerned with improving some heats of reaction derived from high-temperature equilibria. We may write

$$\Delta G_T^\circ = -\boldsymbol{R}T \ln K_{p,T} \quad . \quad . \quad . \quad . \quad (9)$$

where ΔG_T° is the standard Gibbs free-energy change corresponding to the equilibrium constant K_p, both referring to T° K. Since (the Gibbs–Helmholtz equation)

$$\Delta G_T^\circ = \Delta H_T^\circ - T.\Delta S_T^\circ$$

$$\Delta G_T^\circ = (\Delta H_T^\circ - \Delta H_0^\circ) - T(\Delta S_T^\circ - \Delta S_0^\circ) + \Delta H_0^\circ - T.\Delta S_0^\circ \quad . \quad (10)$$

where the subscript 0 refers to 0° K.

If we know the two terms in parentheses and ΔS_0°, the entropy change at absolute zero, we can obtain ΔH_0°, the heat of reaction at absolute zero (and ΔH_X° the heat of reaction at any desired intermediate temperature). For a condensed phase $H_T^\circ - H_0^\circ$ must be determined by a graphical integration :

$$H_T^\circ - H_0^\circ = \int_0^{T'} C_p.\mathrm{d}T + \Delta H' + \int_{T'}^{T''} C_p.\mathrm{d}T + \Delta H'' + \int_{T''}^{T'''} C_p.\mathrm{d}T \quad . \quad (11)$$

for example, where $\Delta H'$, $\Delta H''$ are the heat content changes due to phase changes (melting, crystalline transitions, occurring at T', T'', etc.). For a gaseous phase C_p can be calculated from well-known formulæ of quantum statistics. Similarly, $S_T^\circ - S_0^\circ$ can be computed from the same data needed for $H_T^\circ - H_0^\circ$ for condensed phases, and for gases from other well-known formulæ of quantum statistics. Such computations, though sometimes tiresome, are quite straightforward, the only difficulties coming from corrections for quantum weight and for electronic excitation (of atomic vapours in particular).

Alternatively, one can tabulate by the same means values of $G_T^\circ - H_0^\circ$, or $-(G_T^\circ - H_0^\circ)/T$, the function called " free-energy function " by United States authors ; this is often simpler in practice. We are concerned essentially with $\int_0^T (H_T^\circ - H_0^\circ)\mathrm{d}T/T^2$, and the inverse-square dependence on temperature inside the integral implies that the uncertain high-temperature ranges in determinations in H are not of the importance which one might at first suppose.

It may be of use to quote a few general references on these computations. (*a*) *Theory.* A logical account, particularly on the quantum-weight difficulties, is given by Fowler and Guggenheim.[35] Another general account, from a more directly practical point of view, is given by J. G. Aston.[36] (*b*) *Fact.* A full and accurate survey of numerical data for inorganic substances has been given in a series of memoirs by K. K. Kelley under the

[35] " Statistical Thermodynamics ", C.U.P., 1939, Chap. V.

[36] See H. S. Taylor and S. Glasstone, " Treatise on Physical Chemistry ", Van Nostrand Co., New York, 1942.

general title " Contributions to the Data of Theoretical Metallurgy ".[37] A survey of the heats of vaporisation and free-energy functions of elements, oxides, halides, nitrides, and carbides has been published by L. Brewer and his co-workers,[38] based largely on Kelley's work brought up to date. The particular case of the vapour pressure of metals has also independently been discussed by Eucken.[39] In some cases these discussions make major alterations to the values for heats of atomisation quoted by Bichowsky and Rossini.[21a] Finally, one may refer to a useful list of the quantum weights and excitation energies of low-lying atomic energy states in Landolt–Börnstein's " Tabellen " (Ergänzungsband IIIc).

As particular examples of these methods we shall here consider : (*a*) the heat of atomisation of silicon (and the heat of formation of silicon carbide) ; (*b*) the heat of atomisation of tin ; (*c*) the heat of atomisation of germanium ; (*d*) the heat of formation of silicon monoxide, SiO, and its dissociation energy into atoms.

(*a*) **Heat of Vaporisation of Silicon.**—The vapour pressure of this element has been measured by a streaming technique by von Wartenberg,[40] whose results are only approximate, by Ruff and his co-workers by their spring-balance technique,[41] and by Baur and Brunner,[42] using a mercury-drop null manometer. From a graphical second-law treatment one obtains for λ_0, the heat of vaporisation of the solid at 0° K, the values (44), 150, and 106 kcal., respectively, and it is evident that the second-law method gives only the roughest estimate. To use the third-law method we need data on the specific heat and heat of fusion of silicon. For low temperatures (20—300° K) we have data by Andrews [43] in good agreement with older data by Nernst and Schwers ; [44] the extrapolation from 20° K to absolute zero has been made by taking silicon to be a Debye solid with $\theta_D = 460°$ K. From room temperature to 100° C there are several values quoted in Mellor's treatise, [44a] which have been plotted graphically. Above room temperature to 1200° K we have Magnus's data [45] for the total heat content above 300° K on a sample of known purity. Silicon melts at 1688° K (1415° C) and the range from 1200° to 1688° has been estimated by a graphical extrapolation of Magnus's data. The thermodynamic functions so obtained

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[37] United States Department of the Interior, Bureau of Mines Bulletins : (*a*) 1935, No. 383 (vapour pressures) ; (*b*) 1936, No. 393 (heats of fusion) ; (*c*) 1949, No. 476 (high-temperature heat content, heat capacity, and entropy data) ; (*d*) 1950, No. 477 (revision of entropy data).

[38] In National Nuclear Energy Series, IV, 19B, " Chemistry and Metallurgy of Miscellaneous Materials : Thermodynamics ", edited by L. L. Quill, McGraw Hill, 1950.

[39] *Metallwirtsch.*, 1936, **15**, 27, 63.

[40] *Z. anorg. Chem.*, 1913, **79**, 71.

[41] *Trans. Amer. Electrochem. Soc.*, Preprint 68–32 (1935) ; *Z. Elektrochem.*, 1926, **32**, 515.

[42] *Helv. Chim. Acta*, 1934, **17**, 958.

[43] *J. Amer. Chem. Soc.*, 1930, **52**, 2301.

[44] *Sitzungsber. Preuss. Akad. Wiss.*, 1914, 355.

[44a] " A Comprehensive Treatise on Inorganic and Theoretical Chemistry ", Vol. VI, Longmans, Green and Co., London, 1925.

[45] *Ann. Physik*, 1923, **70**, 303.

were in excellent agreement with those deduced by Kelley [37] from essentially the same data.

The heat of fusion and specific heat of liquid silicon are not precisely known. The heat of fusion may be estimated from the depression of freezing point by metallic solutes ; Kelley [37] so obtains the value 9470 cal./mole ; Kubaschewski *et al.*[46] from similar evidence recommended 11,100 ± 500 cal./mole. The specific heat C_p of liquid silicon is also not well known ; it can hardly be less than 7 cal./g.-atom, and direct experiment suggests the much higher value 11·2 cal./g.-atom.[47] In spite of these uncertainties, the differences implied for λ_0 are small compared with the discrepancies in the second-law treatment. Thus in the following Table the heat of vaporisation λ_0 of silicon at 0° K has been calculated on two assumptions : (*a*) C_p, liquid Si = 7 cal./g.-atom, latent heat of fusion 9470 cal./g.-atom ; (*b*) C_p, liquid Si = 11·2, latent heat 11,200 cal./g.-atom.

Authors	T, ° K	P, mm.	λ_0 (*a*)	λ_0 (*b*)
			kcal /g.-atom	
Ruff *et al.* (grouped data)	2607	752	(84·2)	(82·4)
	2442	147	(87·6)	(86·2)
	2373	70	88·9	87·7
	2309	31	90·5	89·4
	2277	23	90·7	89·8
Baur and Brunner	2160	15	88·5	87·8
	2071	6·3	88·9	88·3
	1980	2	90·0	89·6
	Mean of last six :		89·6	88·8

It can be seen that the values obtained for ΔH_0° are fairly steady except at the very highest temperatures ; by analogy with carbon,[48] one would expect participation of Si_2 molecules at the highest pressures. Similar calculations on the earlier approximate data of von Wartenberg [40] suggest $\lambda_0 \simeq 75$ kcal./mole, as opposed to the second-law value of 44 kcal. We may therefore take a value of 89·2 (± 3·0 perhaps) for the heat of vaporisation of silicon at absolute zero, corresponding to 89·9 kcal. at room temperature (18° or 25°). This calculation has been presented at some length to show the power of the method even when the high-temperature thermal data are only approximate.

The Heat of Formation of SiC (Carborundum).—Ruff [41] also quotes data for the vaporisation of SiC by the reaction

$$\mathrm{SiC_{solid}} \longrightarrow \mathrm{C_{graphite}} + \mathrm{Si_{vapour}}$$

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[46] *Z. Elektrochem.*, 1950, **54,** 275.

[47] Chipman and Grant, *Trans. Amer. Soc. Metals*, Preprint No. 28, 1942.

[48] Brewer, Gilles, and Jenkins, *J. Chem. Phys.*, 1948, **16,** 797.

at temperatures between 2579° and 2925° K. The thermodynamic functions of graphite have been listed up to 1500° K by Rossini and his co-workers,[49] and those of carborundum by Kelley [37, 50] up to 1700° K. In both cases the " free energy function " $-(G^\circ_T - E^\circ_0)/T$ is very well given by a formula of the type $A + BT - CT^2$ from 500° K upwards. Extrapolating these formulæ up to 2500—3000° K, one can obtain a rough estimate of ΔH°_0 for the reaction given as shown in Table 4. From this and the value just obtained

TABLE 4. *Vapour pressure of silicon over carborundum (grouped results)*

T, ° K	V.p., mm.	ΔH°_0	T, ° K	V.p., mm.	ΔH°_0
2579	1·24	126·5	2841	15·9	125·6
2683	6·05	123·4	2925	31·2	125·7
					125·3 Mean

$$\mathrm{Si_{solid}} \rightarrow \mathrm{Si_{vapour}}\,;\quad \Delta H^\circ_0\ 89{\cdot}2$$

we deduce

$$\mathrm{Si_{solid}} + \mathrm{C_{graphite}} \rightarrow \mathrm{SiC_{solid}} : \Delta H^\circ_0 - 36{\cdot}1 \text{ kcal.}$$

$$\text{or}\quad \mathrm{Si_{solid}} + \mathrm{C_{diamond}} \rightarrow \mathrm{SiC_{solid}} : \Delta H^\circ_{291} - 35{\cdot}8 \text{ kcal. } [\equiv - Q_f(\mathrm{SiC})]$$

This value should be equal to $-Q_{f,\,291°}$ listed by Bichowsky and Rossini,[21a] who recommend $Q_{f,\,291} = 28$ kcal./mole as a mean of widely different values (the calorimetric data depend on small differences in large heats of reaction).

If Si and C were of equal " thermal electronegativity " one would predict, from the distances given in Section II, a Si–C distance of 1·944 Å in SiC. The observed value [51] is 1·888 Å. This contraction being interpreted as due to difference in electronegativity (Schomaker–Stevenson), this difference would, from Fig. 3 (equation 8) be equal to 0·49 (Pauling recommends 0·7, the $I + E$ data in Table 2 and equation 7 give 0·7). An electronegativity difference of 0·49 would predict, from Fig. 1, an ionic resonance energy R_{xy} of 5·3 kcal. per bond, or $Q_f(\mathrm{SiC}) = 21$ kcal.; a difference 0·70 would predict $Q_f(\mathrm{SiC}) = 44$ kcal. The agreement is reasonably satisfactory.

(*b*) **Heat of Vaporisation of Tin.**—The vapour pressure of tin has been observed by several workers. (i) Greenwood,[52] by varying the pressure of an inert gas and measuring the temperature of visible ebullition of the liquid metal. Range: temperature 2243—2543° K, pressure 101—760 mm. (ii) Ruff and his co-workers,[53] by their " spring-balance " technique. Range: temperature 2278—2543° K, pressure 126—755 mm. These are in excellent agreement with (i). (iii) Baur and Brunner,[42] by the same technique as used for silicon. Range: temperature 1585—2103° K, pressure

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[49] *Bull. Bur. Stand.*, Circular 461, 1947.

[50] *J. Amer. Chem. Soc.*, 1941, **63,** 1137.

[51] Taylor and Laidler, *J. Appl. Physics*, 1950, **1,** 178.

[52] *Proc. Roy. Soc.*, 1909, *A*, **82,** 396; 1910, **83,** 483.

[53] Ruff and Bergdahl, *Z. anorg. Chem.*, 1919, **106,** 76; Ruff and Mugdan, *ibid.*, 1921, **117,** 147.

2·6—81·7 mm. (iv) Von Wartenberg [54] obtained two isolated values from the rate at which tin is carried as vapour by a stream of nitrogen : 1403° K, $p = 0{\cdot}13$ mm. ; 1633° K, $p = 1{\cdot}2$ mm. (v) Harteck [55] at 1264—1434° K and pressures of 5×10^{-6} to $8{\cdot}5 \times 10^{-4}$ mm. by Knudsen's technique of effusion through a small hole. (vi) Granovskaya and Lyubimov [56] have measured the vapour pressure by Langmuir's method (rate of evaporation from a surface). Range : temperature 1003—1213° K, pressure $1{\cdot}4 \times 10^{-6}$ to 3×10^{-4} mm.

We have here therefore data by various authors, by different techniques, covering a range of 1500^0 and a factor about 10^8 in pressure. As before, attempts to deduce a second-law value for the heat of vaporisation lead to wide discrepancies. In the range round 100 mm. the data of the first three investigations quoted agree very well, and so do the two sets of data between 100 and 760 mm. (see Fig. 4). At lower temperatures considerable scatter is apparent and the results of (v) and (vi) are quite incompatible. On application of a third-law calculation to these data the situation becomes clearer. We have throughout *assumed* the vapour to be monatomic, correcting therefore Harteck's data, and used the thermodynamic functions listed by Kelley.[37] For tin, whose melting point is so low (505° K), the heat of fusion is well established, but the specific heat of the liquid metal is, once more, very uncertain. The computations have therefore been carried through for four constant values of C_p 7·0, 7·3 (favoured by many previous authors), 9·0, and 11·0 (improbably high) as an illustration of the effect of errors in this quantity. In view of the large numbers of experimental points we have here taken smoothed values by plotting p against

TABLE 5

Authors	T, ° K	p, mm.	λ_0 calc. for different values of C_p for liquid tin :				p, mm , calc.
			$C_p = 7$	7·3	9	11	
Ruff *et al.* Greenwood	2500	590	63·4	62·8	59·4	55·4	638
	2400	316	63·9	63·3	60·2	56·5	385
	2300	162	64·3	63·8	60·9	57·5	220
Baur and Brunner	2100	78	61·9	61·5	59·2	56·4	63·1
	2000	46	61·2	60·8	58·6	56·1	30·6
	1800	13	59·6	59·3	57·6	55·7	5·60
	1600	2·9	58·0	57·8	56·5	55·0	0·67
v. Wartenberg .	1504	0·39	60·8	60·7	59·6	58·3	0·17
Harteck . . .	1400	$8{\cdot}9 \times 10^{-4}$	73·4	73·3	72·4	71·3	$4{\cdot}4 \times 10^{-2}$
	1300	$1{\cdot}7 \times 10^{-4}$	72·6	72·4	71·7	70·8	$8{\cdot}3 \times 10^{-3}$
Granovskaya and Lyubimov	1200	$2{\cdot}9 \times 10^{-4}$	65·8	65·7	65·4	64·4	$1{\cdot}2 \times 10^{-3}$
	1000	$1{\cdot}45 \times 10^{-6}$	65·8	65·7	65·1	65·0	$7{\cdot}4 \times 10^{-6}$

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[54] *Z. Elektrochem.*, 1913, **19**, 482.
[55] *Z. phys. Chem.*, 1928, **134**, 1.
[56] *J. Phys. Chem. U.R.S.S.*, 1944, **22**, 527.

$1/T$ for each of the references given; the data of Greenwood and of Ruff and his co-workers agree so well that they have been considered together. The results are in Table 5.

It is clear from these data that Harteck's results are incompatible with the other results which are in fairly good mutual agreement. The mean values of λ_0 for the other work (double weight being given to the concordant high-temperature results) are: for $C_p = 7$, 61·8; $C_p = 7{\cdot}3$, 62·4; $C_p = 9{\cdot}0$, 60·2; $C_p = 11$, 57·7 kcal./g.-atom. The best estimate is probably $\lambda_0 = 62{\cdot}4 \pm 2{\cdot}0$ kcal./g.-atom, and the probable error could be reduced to about a third if the specific-heat data were certain.

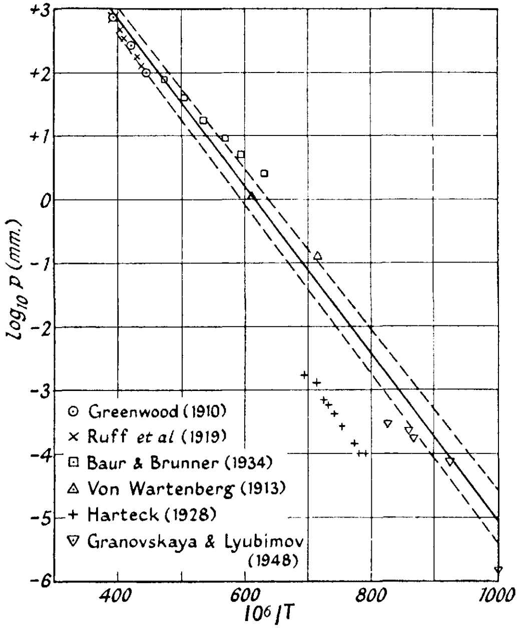

FIG. 4

The full line shows the third-law calculation for $\lambda_0 = 62$ *kcal.; the broken lines for* $\lambda_0 = 60$ *and* 64.

In Fig. 4 therefore we have plotted the vapour-pressure curve corresponding to $\lambda_0 = 62{\cdot}4$ (broken lines $\pm$ 2·0 kcal.), $C_p = 7{\cdot}3$, the vapour pressures corresponding to this being given in the last column of Table 5. The agreement is sufficiently satisfactory for discrepancies to be worth special comment.

(*a*) The accuracy of Greenwood's data is noteworthy. These results have been much criticised as being seriously affected by porosity in the crucibles used, but Partington [57] has recently denied that the crucibles

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[57] "Advanced Treatise on Physical Chemistry", Longmans, Green and Co., London, 1950, Vol. II, p. 237.

used *were* in fact appreciably porous. In agreement with Partington, our analysis shows Greenwood's data to be not seriously in error.

(*b*) Fig. 4 suggests that Baur and Brunner's results are systematically too high at lower pressures, and that second-law estimates based on these alone [58] are untrustworthy. Eucken [39] points out the same systematic trend in their work on Ag, Be, Al, and Mn and mentions that Fischer [59] has explained such an effect as probably due to the peculiarities of their pressure-measurement device.

(*c*) It remains to consider Harteck's data.[55] Here, as Table 5 shows, the vapour pressure observed is about 50 times too low. One can only suppose that in some circumstances (surface impurities ?) tin is peculiarly difficult to vaporise. This hypothesis gains some support from the early work of von Wartenberg [60] on the vapour density of tin, which is often quoted as evidence for the vapour's being Sn_4. Actually, however, no constant value was obtained for the atomicity of the vapour, the best integral value corresponding roughly to Sn_7 (!) and von Wartenberg quotes the molecular weights as " naturally only apparent ". These two researches suggest that tin vapour is *not* necessarily polyatomic, but that peculiar difficulties sometimes attend attainment of equilibrium on vaporisation.

The good agreement of all the other data with the third-law computations, in which a monatomic vapour was *assumed*, argues strongly for the vapour's being monatomic, in analogy with lead.

(*c*) **The Heat of Vaporisation of Germanium.**—Only one study of the vapour pressure of pure germanium has so far been published, that by Searcy [61] using Knudsen's technique between 1510° and 1882° K. These data were treated by Searcy by second-law methods, giving

$$\mathrm{Ge_s} \longrightarrow \mathrm{Ge_{vapour}} : \Delta H^{\circ}_{298} = 84{\cdot}0 \pm 1{\cdot}5 \text{ kcal.}$$

Recently, by using the extremely pure germanium now of great industrial importance, two independent series of measurements have been published on the specific heat between liquid-helium temperatures and 160—200° K, by Estermann and Weertman [62] and by Hill and Parkinson.[63] These two sets of results are in good agreement. Up to 200° K the errors in the thermodynamic functions of germanium are therefore very small. From 200° K to the melting point, T_m (1232° K), the Reviewer has calculated C_v from Debye's equation ($\theta = 400°$) and $C_p - C_v$ from the empirical equation

$$C_p - C_v \propto C_p^2 T/T_m$$

the curve so obtained agreeing fairly well with Kelley's estimate [37] of $C_p = 4{\cdot}62 + 2{\cdot}27 \times 10^{-3}T(273\text{—}713° \text{K})$.

The heat of melting has been estimated by Kubaschewski [46] at 7·3 kcal./g.-atom and no data exist on the specific heat of the liquid, which has been assumed to be 7·3 cal./g.-atom (analogy with tin). The high-temperature range in the " free-energy function " is thus uncertain. Taking

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[58] Long and Norrish, *Phil. Trans.*, 1949, **241,** *A*, 587.

[59] *Helv. Chim. Acta*, 1935, **18,** 1028.

[60] *Z. anorg. Chem.*, 1908, **56,** 320.

[61] *J. Amer. Chem. Soc.*, 1952, **74,** 4789.

[62] *J. Chem. Physics*, 1952, **20.**

[63] *Phil. Mag.*, 1952, **43,** 309.

the probable errors as (i) 0—200° K, negligible, (ii) 200—1232° K, ± 10%, (iii) 1232—1700° K (mean value of v.p. data), ± 30%, one obtains an error of ± 4 kcal. in ΔH_0° if the errors in (ii) and (iii) are of the same sign. A check on the consistency of the data involves a much smaller error, since the range 200—1500° K is common.

The computation of ΔH_0° is then as shown in the following Table (smoothed data):

T, ° K	1500	1600	1700	1800	1900
$\log_{10} p$ (atm.) . . .	−6·01	−5·24	−4·56	−3·96	−3·43
ΔH_0°	89·0	88·9	88·8	88·6	88·5

as a mean value one may recommend ΔH_0°(vap.) = 88·8 (± 4·0) and ΔH_{291}°(vap.) = 89·2 (± 4·0) kcal./g.-atom. The self-consistency of the data and the good agreement with the second-law value show that this unique set of data can be accepted with confidence; once more the value of ΔH_0° could be much improved if more were known about high-temperature specific heats.

The lack of high-temperature specific heat data on liquid metals is indeed in general a limiting factor to the accuracy of deduction of many heats of reaction. Such data as are available [64] suggest a remarkable constancy in C_p.[65] Simple theory would predict only a high-temperature constancy in the lattice contribution to C_v; but to this must be added two terms: (i) The electronic specific heat, which theoretically is proportional to T; at very low temperatures (liquid helium) this term is *greater* than the lattice term since the latter is then proportional to T^3; at room temperatures it is negligible, and at high temperatures it becomes again appreciable since it continues to increase while the lattice term remains constant. (ii) The difference $C_p - C_v$, which must be positive and can be calculated from coefficients of expansion and compressibility; if C_p therefore really is roughly constant, C_v must be *decreasing*. This decrease has been observed for mercury and the alkali metals.[66] It can be shown that such a decrease is incompatible with simple harmonic vibrations,[67] so that the study of high-temperature C_v might throw light on problems of the liquid state, as well as being of practical importance.

Finally, one may point out that the heats of vaporisation of silicon and germanium are practically identical. In Group IIA also the heat of vaporisation of magnesium is *less* than those of both Be and Ca. It is not therefore always possible simply to interpolate heats of vaporisation as a function of interatomic distance, even in the same sub-group of the Periodic Table.

(*d*) **The Heat of Formation and Dissociation Energy of SiO.**—Silicon monoxide has been known as a " spectroscopic " molecule for some time.

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[64] See, *e.g.*, Van Arkel, " Reine Metalle ", Springer-Verlag, Berlin, 1939.

[65] Cf. also the comments of Sir Andrew McCance, *Discuss. Faraday Soc.*, No. 4, 1948, p. 8.

[66] Eyring and Kincaid, *J. Chem. Phys.*, 1937, **5**, 591.

[67] Cf. Fowler and Guggenheim, ref. 35, p. 147.

It has been studied by Bonhoeffer [68] and more recently by Barrow and his co-workers.[69] The equilibrium distance (1·510 Å) and the fundamental frequency of vibration (1242 cm.$^{-1}$) are well known and estimates have been made of its dissociation energy. More directly chemical evidence shows that silica is unusually volatile in the presence of reducing agents (silicon itself, or hydrogen, for example) and powdery or resinous sublimates have been obtained of approximately the composition SiO, although *X*-ray investigation showed many of these solid products to be intimate mixtures of silicon and silica, produced presumably by disproportionation. The solubility of silica in molten iron points to the existence of SiO as a solute ; [70] it is possible to reduce silicates to oxides and SiO by heating them with silicon, and even some oxides to metals and SiO, *e.g.*,

$$Nb_2O_5 + 5Si \rightarrow 2Nb + 5SiO \text{ (vapour)},$$

and SiO *may* exist as a solid chemical species.[71]

We now use some data on high-temperature equilibria to compute by statistical methods the heat of formation of SiO vapour, and hence deduce the dissociation energy. The reactions are :

$$H_2 \text{ (gas)} + SiO_2 \text{ (quartz)} \rightarrow H_2O \text{ (gas)} + SiO \text{ (gas)}$$
$$Si \text{ (solid)} + SiO_2 \text{ (quartz)} \rightarrow 2\ SiO \text{ (gas)}$$

and the " free-energy functions " required have been obtained as follows : H_2, H_2O, from publications of the Bureau of Standards ; [49] SiO_2, from Mosesman and Pitzer's data ; [72] SiO, calculated by the usual simple-harmonic rigid rotator approximation (symmetry number unity) ; Si, as already explained.

The first of these reactions was studied between 1200° and 1500° C by a streaming technique by Grube and Speidel,[73] who determined the SiO content of the gas by decomposing it on an iron wire and analysing the product for silicon. By second-law methods they found a mean $\Delta H^\circ_T = 112 \pm 6$ kcal. This is in reasonable agreement with the third-law calculations as shown in the following Table ($p_{H_2} = 1$ atm.).

T, ° K	p_{SiO}, mm.	ΔG°_T	$-(\Delta G^\circ_T - \Delta H^\circ_0)$	ΔH°_0(kcal./mole)
1473	0·05	59·3	73·9	133·3
1573	0·09	56·6	78·6	135·2
1673	0·28	52·5	83·1	135·6
1773	0·62	51·4	87·8	(139·2)
			Mean of first three :	134·7

The discrepancy of the highest-pressure point would suggest that the method of analysis begins to break down and that about one-third of the SiO escaped detection. These observations are supported by the recent

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[68] *Z. phys. Chem.*, 1928, **131,** 363.
[69] For data see Herzberg, ref. 18.
[70] Zapffe and Sims, *Amer. Inst. Min. Met. Eng.*, Technical Publication No. 1498, 1942.
[71] Zintl, Braüning, Grube, Krings, and Morawietz, *Z. anorg. Chem.*, 1940, **245,** 1.
[72] *J. Amer. Chem. Soc.*, 1941, **63,** 2352.
[73] *Z. Elektrochem.*, 1949, **53,** 339.

work of Tombs and Welch,[74] who analysed the gas stream for H_2O by thermal conductivity. Here, as these authors point out, the obvious risk is that some water may be coming out of the glass, etc. In the following table, a third-law calculation is shown for their data—the 23 observations given fall naturally into 5 groups.

T, ° K	No. of observations	ΔG°_{T}	$-(\Delta G^{\circ}_{T}-\Delta H^{\circ}_{0})$	ΔH°_{0}	ΔH°_{0} (corr)
1508	2	47·5	75·1	122·6	129·7
1632	4	43·7	80·7	124·4	125·8
1744	6	41·3	85 8	127·1	127·8
1836	5	40 4	89·7	130·1	130·5
1904	6	37·6	92 6	130 2	130·4

The value for ΔH°_{0} shows a considerable drift, but tends to become steady at the highest pressures, where the effect of such adventitious water would be least. If one corrects the data assuming a constant adventitious water pressure of $0{\cdot}2 \times 10^{-4}$ atm., an almost constant ΔH°_{0} value is obtained (last column of the Table above). A " best " value of $\Delta H^{\circ}_{0} = 130{\cdot}3$ may be recommended.

We now turn to the reaction Si (solid) + SiO_2 (quartz) $\longrightarrow$ 2SiO (gas). This was studied by following loss of weight by Knudsen's method by Schäfer and Hörnle,[75] whose results are analysed in Table 6. The agreement is extremely satisfactory. Tombs and Welch [74] have also studied this reaction by measuring the weight-loss from a boat in a stream of argon ; their results are shown in Table 7. By condensing the SiO as a solid on to a weighed alumina tube, these authors were also able to follow the reaction to higher temperatures where direct weight loss was impracticable through spattering of liquid silicon ; these results are shown in the following Table.

TABLE 6

T, ° K	ΔG°_{T}	$-(\Delta G^{\circ}_{T}-\Delta H^{\circ}_{0})$	ΔH°_{0}
1336	55·1	109·7	164·8
1367	52·7	112·1	164·8
1398	50·2	114·5	164·7
1429	47·7	117·0	164·7
1460	46·2	119·4	(165·6)
			Mean 164·7

TABLE 7

T, ° K	ΔG°_{T}	$-(\Delta G^{\circ}_{T}-\Delta H^{\circ}_{0})$	ΔH°_{0}
1573	37·0	128·3	165·3
1623	34·6	132·2	166·8
1653	33·1	134·5	167·6
1713	30·2	139·0	169·2
			Mean 167·2

T, ° K	ΔG°_{T}	$-(\Delta G^{\circ}_{T}-\Delta H^{\circ}_{0})$	ΔH°_{0}
1773	26·9	143·2	170·1
1853	23·4	148·4	170·8
1920	19·8	153·1	172·9
			Mean 171·2

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[74] *J. Iron Steel Inst.*, 1952, **172,** 69.

[75] *Z. anorg. Chem.*, 1950, **263,** 261.

The correctness of the " free-energy functions " being assumed, therefore, these data give the heats of certain reactions involving the gaseous SiO molecule. All the other heats of formation are known, so the data can be corrected to 291° K to give $\Delta H_f(-Q_f)$ of SiO at this conventional standard temperature. Taking Q_f for H_2O (gas) as 57·8 [21a] and that for solid quartz as 210·3 kcal./mole,[76] we can compute the heat of formation of SiO (see Table 8).

TABLE 8

Reaction	Authors	Technique	ΔH_0°	ΔH_{291}°	$Q_f(SiO_G)$ $(-\Delta H_f, 291°)$
$H_{2G} + SiO_2 \longrightarrow H_2O_G + SiO$	G. & S.	Si analysis	134·7	135·4	17·1
	T. & W.	H_2O analysis	130·3	131·0	21·5
$Si + SiO_2 \longrightarrow 2SiO$ . . .	S. & H.	Weight loss	164·7	166·3	22·0
	T. & W.	Weight loss	167·2	168·8	20·8
	T. & W.	Analysis of gases	171·2	172·8	18·8

Schäfer and Hörnle's data, which internal consistency suggests to be the most precise, are in good agreement with two of the sets of Tombs and Welch's data ; their third method and that of Grube and Speidel involve difficult analytical techniques based on heterogeneous reactions and give a slightly lower result. We may take

$$Q_f \text{ (SiO, gas) at } 291° \text{ K} = 21{\cdot}6 \pm 1 \text{ kcal.}$$

whence

$$Si_{crystal} + O \longrightarrow SiO\,; \quad \Delta H_{291°} = -80{\cdot}7, \quad \Delta H_0 = -80{\cdot}6$$

Adding to this the heat of vaporisation of silicon at absolute zero, we obtain

$$D_0^\circ \text{ (SiO)} = 170 \pm 6 \text{ kcal. (7·39 volts)}$$

In an important recent paper, where such third-law methods are applied to several oxides, Brewer and Mastick [77] have deduced a value of about 165 kcal./mole from other experimental data.

From linear Birge–Sponer extrapolation of the $^1\Sigma$ ground state,[18] one obtains 7·8 volts for the dissociation energy of SiO (private communication from Dr. R. F. Barrow) ; Gaydon [17] recommends 8 ± 1 volts, and Vago and Barrow [78] 8·26. In all cases these authors assume the products of dissociation to be ground-state atoms.

In this calculation we have used third-law methods to compute an uncertain dissociation energy of a diatomic molecule. A combination of third-law and spectroscopic methods on SnO has recently been published by Drummond and Barrow.[79] In their paper, a dissociation limit in SnO of

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[76] Humphrey and King, *J. Amer. Chem. Soc.*, 1952, **74**, 2041.

[77] *J. Chem. Phys.*, 1951, **19**, 834.

[78] *J. Chim. physique*, " Contrib. étude structure mol., Vol. commém. Victor Henri ", Desoer, Liège, 1947, p. 201.

[79] *Proc. Phys. Soc.*, 1952, *A*, **65**, 148.

uncertain " identification " has, by third-law evaluation of the heat of vaporisation of SnO, and the calculations on Sn given in this present paper, been identified as very probably due to the process

$$\text{SnO ("}E\text{-state")} \longrightarrow \text{Sn } ({}^3P_2) + \text{O } ({}^3P)$$

and hence, not only is it almost certain that SnO dissociates into ground-state oxygen and the triplet ground-state of tin, but also the particular component of the tin triplet-state has been identified, giving D_0^0 (SnO) = 121 kcal. (5·25 volts). Brewer and Mastick [77] have also by third-law methods obtained a dissociation energy D_0^0 for PbO of 98 kcal. (4·25 volts). SiO, SnO, and PbO probably dissociate therefore into the ${}^3P$ ground states of Si, Sn, Pb ; if CO does the same, then the high value 170 kcal. for the heat of vaporisation of carbon follows.

Section IV

Before considering the bond energies and equilibrium properties of molecules containing the elements C, Si, Ge, Sn in different valencies we shall, in the present Section, discuss briefly the effect of van der Waals interaction between the " non-bonded " atoms. Again, the tetrahalides of Group IV—IV_B are a particularly suitable subject of investigation.

The structure of such molecules as NH_3 is largely determined by repulsion between the bonds and the " lone-pair " electrons ; [80] but for carbon, silicon, etc., there are no lone-pairs to complicate the picture.

Previous discussions on these repulsive forces have mainly considered their effect on the vibrational frequencies of the molecule. By representing the repulsion as an inverse power-function of distance, it is possible to represent adequately the frequencies, which otherwise do not agree with the simple valency-force field (S.V.F.F.) model. The laws of non-bonded repulsive force so deduced agree very roughly with other approximate estimates —the force between " non-bonded " chlorine atoms being considered to be the same as between argon atoms at the same distance, for example.[81, 82] But the extension of these arguments has led to improbable consequences. Heath and Linnett,[12] for example, deduce that the C–Cl distance in CCl_4 is stretched by no less than 0·49 Å by the repulsion between the Cl atoms. This conclusion, which cannot be reconciled with the C–Cl distances in CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 [1·781, 1·77 (± 02), 1·761, 1·765 (± 0·015), respectively] [20, 83] or with the approximate constancy of the successive substitution heats of CH_4 with Cl,[1] could, however, well arise from extrapolation of an unduly simplified potential energy function.

We shall here, therefore, invert the problem and consider whether from what is *known* about potential-energy functions of " non-bonded " atoms one can deduce (*a*) the " non-bonding " force-constants in the actual mole-

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[80] *Fact* : Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 153. *Theory* : Cf. Lennard-Jones and Pople, *Discuss. Faraday Soc.*, 1951, **10**, 9.

[81] Urey and Bradley, *Phys. Reviews*, 1931, **38**, 1969.

[82] Heath and Linnett, *Trans. Faraday Soc.*, 1948, **44**, 561.

[83] Micro-wave data listed in *Ann. Rev. Physical Chem.*, Vols. 1 and 2 (1950, 1951), Annual Reviews, Inc., Stanford, California.

cules,[81, 82] (*b*) the heats of formation of such molecules [the arguments in Section II suggest that the effect of repulsion is small (cf. Pauling, ref. 4)], (*c*) the observed interatomic distances—in particular the peculiar discrepancy of carbon–halogen bond lengths.

From London's theory of van der Waals forces we know that the attractive potential energy can be approximately represented as an inverse sixth-power function of the interatomic distance y, while the repulsive potential energy is more nearly an exponential function. To simplify the mathematics it is usual to replace this also by a high-power law, giving for the " non-bonding " potential energy W

$$W = -\alpha/y^m + \beta/y^n \qquad . \quad . \quad . \quad . \quad (12)$$

where $m = 6$. This model has been successfully applied by Lennard-Jones, with $n \simeq 12$,[84] to the second virial coefficient of gases, and by Lennard-Jones and Devonshire [85] to the equation of state of condensed phases of the inert gases.

In our discussion we shall be concerned with W, $\mathrm{d}W/\mathrm{d}y$, and $\mathrm{d}^2W/\mathrm{d}y^2$. It is convenient to transform all these in terms of W_0, the equilibrium energy, and Y_0, the equilibrium distance—where the repulsive and attractive forces are equal and opposite—by using the relation

$$(\mathrm{d}W/\mathrm{d}y)_{y=Y_0} = 0 \qquad . \quad . \quad . \quad . \quad (13)$$

From (12) and (13) we can easily deduce that

$$W_0 = \frac{-\alpha}{Y_0{}^m}\left(\frac{n-m}{n}\right) = \frac{-\beta}{Y_0{}^n}\left(\frac{n-m}{m}\right) \qquad . \quad . \quad . \quad (14)$$

whence

$$W = W_0\left(\frac{n\gamma^m}{n-m} - \frac{m\gamma^n}{n-m}\right) = W_0\psi(\gamma) \quad . \quad . \quad . \quad (15)$$

$$\frac{\mathrm{d}W}{\mathrm{d}y} = \frac{W_0}{y}\left(\frac{mn}{n-m}\right)(\gamma^m - \gamma^n) = \frac{|W_0|}{y}\chi(\gamma) \qquad . \quad . \quad (16)$$

$$\frac{\mathrm{d}^2W}{\mathrm{d}y^2} = \frac{W_0}{y^2}\left[\frac{nm}{n-m}(n+1)\gamma^n - \frac{nm}{n-m}(m+1)\gamma^m\right] = \frac{|W_0|}{y^2}\psi(\gamma) \ . \quad (17)$$

where γ is the dimensionless variable *defined* by

$$\gamma \equiv Y_0/y \qquad . \quad . \quad . \quad . \quad . \quad (18)$$

If we assume given values for m (= 6) and n (= 12), then ϕ, χ, and ψ can once and for all be calculated as functions of γ ; and y being regarded as an experimental fact, the discussion then involves W_0 and Y_0 only. With this choice of the exponents m and n we have

$$\left.\begin{aligned} \phi(\gamma) &= 2\gamma^6 - \gamma^{12} \\ \chi(\gamma) &= 12\gamma^6 - 12\gamma^{12} \\ \psi(\gamma) &= 156\gamma^{12} - 84\gamma^6 \end{aligned}\right\} \qquad . \quad . \quad . \quad . \quad (19)$$

We start by considering what is known about Y_0—the equilibrium distance of two atoms in *different* molecules. Pauling [4] has, from the empirical data of crystallography, shown that " van der Waals distances "

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[84] *Physica*, 1937, **4**, 941.

[85] *Proc. Roy. Soc.*, 1937, *A*, **163**, 53.

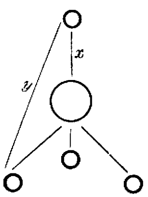
can be roughly dissected into sums of two " van der Waals radii ", and gives the following list of van der Waals radii :

Van der Waals radii, ρ (from Pauling)

Element . .	N	P	As	Sb	O	S	Se	Te	F	Cl	Br	I
Radius (Å) .	1·5	1·9	2·0	2·2	1·40	1·85	2·00	2·20	1·35	1·80	1·95	2·15

($\pm$ 0·05—0·10 Å in each case)

From the geometry of the tetrahedron, $y = 1{\cdot}633x$. The force between the peripheral atoms is repulsive if $y <$ (2 van der Waals radii), *i.e.*, $y = 1{\cdot}633x \leqslant 2\rho$ or $x \leqslant 1{\cdot}22\rho$.



Referring to the experimental data in Table 3, we see that this condition is easily satisfied for CF_4, CCl_4, CBr_4, CI_4, just satisfied for the halides of Si and Ge, and *not* satisfied for those of Sn. The fact that the halides of C show unusually long bonds (Section II) encourages us to more detailed treatment.

Let us now consider W_0, the equilibrium van der Waals energy. This has been computed, together with the equilibrium distance Y_0, for simple gases by Lennard-Jones, using the 6—12 potential.[84] His results are given in Table 9, which also gives as a rough measure of intermolecular energy the latent heat of evaporation, L_v, of the liquid at its boiling point ; it can be seen that for monatomic gases L_v/W_0 is roughly constant at about 6·2, for diatomic gases at about 7·5, from which ratio are deduced the W_0 values quoted in Table 9 for the halogens.

TABLE 9.* W_0 *and* Y_0, *from the* 6—12 *potential ; heats of vaporisation of liquids at the boiling point* (L_V).

	W_0		Y_0, Å	L_v (cal./g.-mol)	L_v/W_0
	10^{-15} ergs	cal /g -atom			
Neon	4·88	70·6	3·049	442	6·38
Argon	16·50	239	3·819	1590	6·25
Krypton . . .	23·84	346	4·030	2010	5·80
Xenon	30·99	447	4·561	3110	6·82
Nitrogen . . .	13·24	192	4·174	1457	7·58
Oxygen	16·97	244·9	—	1858	7·58
CO	13·36	192·8	—	1470	7·60
CH_4	19·70	284·3	—	2040	7·20
F_2	(15·1)	(219)	—	1640	—
Cl_2	(40·7)	(590)	—	4420	—
Br_2	(68·2)	(990)	—	7420	—
I_2	(95·5)	(1385)	—	10390	—

* W_0 and Y_0 for Ne, A, N_2, O_2, CO and CH_4 from Lennard-Jones ; [84] Kr, private communication from Professor J. A. Beattie ; Xe, Beattie, Barriault, and Brierley, *J. Chem. Phys.*, 1951, **19**, 1219 ; L_v values from Kelley.[37b]

The W_0 values for the halogens are considerably greater than the values for the corresponding inert gases. If we assume the *repulsion* energy functions to be the same in the two cases, a simple calculation gives Y_0 for the van der Waals attraction between two non-bonded halogen atoms ; the results are compared in Table 10 with *twice* the Pauling " van der Waals radii " ρ ($\pm$ 0·1—0·2).

TABLE 10

	Y_0, calc.	2ρ		Y_0, calc.	2ρ
F	2·78	2·70	Br	3·69	3·90
Cl	3·54	3·60	I	4·16	4·30

The agreement is satisfactory, and we may now proceed therefore to apply equations (19) for the 6—12 potential, using the W_0, Y_0 values in Tables 9 and 10 (calc. values).

The application to the force constants themselves comes directly from equations (19). In Fig. 5 are compared the force constants so calculated for " non-bonded " chlorines at distances y with those deduced by Heath and Linnett.[82] The two curves agree well for the higher values of the " non-bonding " force constant, so the arguments adduced by Heath and Linnett from vibrational frequencies are roughly confirmed ; it would appear that Heath and Linnett's function over-estimates the effects at longer distances.

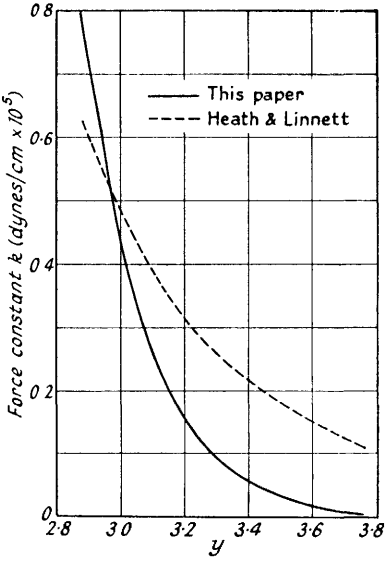


FIG. 5

Comparison of force constants for " non-bonded " chlorine atoms at a distance y *Å.*

We now consider the effect on interatomic distances. For the molecule to be in equilibrium,

$$\sqrt{6}\, \mathrm{d}W/\mathrm{d}y = \mathrm{d}C/\mathrm{d}x \quad . \quad . \quad (20)$$

where C is the " chemical " bond energy acting along x (the C–Cl distance in CCl_4, for example). Suppose the chemical bond to be a harmonic oscillator with force constant k ; then, if Δx is the lengthening of the bond along x due to the repulsion,

$$\sqrt{6}\frac{|W_0|}{y}\chi(\gamma) = k\,\Delta x$$

But for a tetrahedron, $y = 2\sqrt{6}x/3$

therefore $$\Delta x = \frac{3}{2}\cdot\frac{|W_0|}{kx}\cdot\chi(\gamma) \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Taking for the halides of carbon the observed x values quoted in Table 5, and the values of W_0 and Y_0 (and hence γ) just deduced, we can calculate Δx from k, the force constant of the "chemical" carbon–halogen bond. Taking for CF_4 6·5, CCl_4 3·2, CBr_4 2·5, CI_4 2·0 (10^5 dynes/cm.), we calculate that the C–halogen bonds in these molecules are lengthened by repulsion by 0·034, 0·128, 0·152, and 0·180 Å, respectively. Carrying through the same calculation for the silicon halides, we calculate the elongations 0·004, 0·011, 0·028, and 0·032 Å, respectively. For Ge and Sn the elongations calculated are naturally smaller still.

The conclusions thus reached are in satisfactory agreement with the empirical deductions from Fig. 2, *viz.*, that the C–F bond in CF_4 was slightly longer than expected, and that the bonds in CCl_4, CBr_4, CI_4 were all about 0·07 Å too long, while the other tetrahalide bonds show no significant lengthening. The predicted lengthening is roughly twice as large as that deduced from Fig. 2, which is reasonable agreement in view of the approximate nature of the theory used and the sensitiveness of the function used to small changes in γ. It remains therefore to consider the effect of these forces on the total energy of the molecule.

When γ (equation 18) is less than unity, the tendency of the van der Waals forces is to shorten the bonds and increase the bond energy from what would be otherwise expected. For a tetrahedral molecule the maximum such stabilisation energy will be $6W_0/4$ per bond or about 1 kcal. (Table 7); this is a *maximum*, since the contraction of the *non-bonded* distance would usually imply a contraction of the *bonding* distance below the equilibrium value. Comparing, therefore, a tetrahedral molecule XY_n with a diatomic molecule XY, we should find a small correction of the order 1 kcal. per bond; on comparison of one tetrahedral molecule with another, the correction becomes still smaller since the bond energies already contain these van der Waals corrections; and finally, the effect on the means of bond energies is trivial since from the polarisability interpretation of van der Waals attraction energies [86] these also are subject to a geometric-mean rule in the first approximation. These conclusions hold if $\gamma \lesssim 1$.

If $\gamma > 1$ (CCl_4, for example) the corrections become appreciable. As a result of the mutual interaction, the chemical bond is lengthened by Δx and its bond energy lessened by $\frac{1}{2}k(\Delta x)^2$, the van der Waals distance is shortened from Y_0 to a distance $y(\gamma \equiv Y_0/y)$, and the energy of interaction changed from W_0 to $W_0\psi(\gamma)$ (equation 15). Hence the total lessening of the bond energy ΔB is given by

$$\Delta B = \tfrac{6}{4} \mid W_0[\phi(\gamma) - 1] \mid + \tfrac{1}{2}k(\Delta x)^2$$

if we reckon the bond energy from a standard value containing the full W_0 contribution. As Δx is not directly measurable, it is convenient to use equation (21) to deduce

$$\Delta B = \tfrac{6}{4} \mid W_0[\phi(\gamma) - 1] \mid + \tfrac{9}{8} \frac{\mid W_0 \mid^2}{kx^2} \chi^2(\gamma) \qquad . \quad . \quad (22)$$

In this way we calculate from the numerical data already quoted the following values for ΔB for carbon halides (in kcal. per bond): CF_4 $3\cdot_1$ CCl_4 $8\cdot_2$,

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[86] London, *Trans. Faraday Soc.*, 1937, **33**, 8.

CBr_4 6·$_8$, CI_4 11·0. These considerable diminutions in the bond energies may to some extent explain the anomaly in the C–I bond energy.

The theory of this Section has therefore (i) confirmed that a considerable effect on force constants is to be expected, particularly for the halides of carbon ; (ii) confirmed qualitatively and roughly quantitatively the discrepancies of bond lengths in the carbon halides from those predicted by the Schomaker–Stevenson rule ; (iii) confirmed that " non-bonding " repulsive forces in tetrahedral molecules make but little difference to bond energies except, once more, in such cases as the halides of carbon ; and (iv) incidentally confirmed that Pauling's " van der Waals radii " agree well with those calculated by Lennard-Jones's " 6–12 potential " from virial coefficients.

Section V

We now consider together the data available for the internuclear distances, the force constants, and the bond energies (as defined in Section I) for the compounds XY, XY_2, and XY_4 where X is C, Si, Ge, Sn, or Pb, and Y is hydrogen or a halogen. The data are given in Table 11. The bond energies for carbon compounds have been calculated for two values of the latent heat of vaporisation (170 or 125 kcal./g.-atom). The problem which we are trying to illuminate is : to what extent do variations in these three quantities go together (" equilibrium variation ") and to what extent must we consider also " separation variation " ?

We begin by considering the distances $_4r$ in XY_4 and $_1r$ in XY. For CH_4 : CH $_4r/_1r = 0{\cdot}976$; for SiF_4 : SiF 0·96 ; for CF_4 : CF 1·07. From the electronegativity arguments of Section II we calculate for SiH_4 $_4r = 1{\cdot}510$, for SnH_4 $_4r = 1{\cdot}731$, whence for SiH_4 : SiH $_4r/_1r = 0{\cdot}993$, and for SnH_4 : SnH, 0·970. Once more we have a general rule ($_4r/_1r \simeq 0{\cdot}975$) with the carbon halide anomalous, and we may conclude that CF_4 (but *not* SiF_4) has the carbon–halogen bond lengthened by about 0·12 Å [cf. 0·07 Å (Section II), 0·03 Å from the repulsion theory of Section IV].

It has been shown empirically, particularly by Fox and Martin [6] and by Linnett,[8] that, in a series of bonds involving the *same* atoms (C–C, C–H for example), kr^n is constant where $n \simeq 5$. From this rule we would expect, then, the force constants in XY_4 to be $(0{\cdot}975)^{-5} = 1{\cdot}135$ times those in XY. The values so " calculated " (Table 11) are in good agreement with the S.V.F.F. values for CH_4 and SiH_4 where non-bonding repulsion is small, and for the tetrahalides lie between the S.V.F.F. calculations which make no allowance for non-bonding repulsion and Heath and Linnett's calculations which tend to overestimate it (Section IV).

In the same way we might expect the bond energies in XY_4 to be $(0{\cdot}975)^{-3} \simeq 1{\cdot}079$ times more than in XY. Since the bond energies $_4B$ are better known than the spectroscopic dissociation energies $_1B$, we show in Table 11 the " calculated " values of $_1B$. As far as they go, the agreement is satisfactory with one marked exception, that the dissociation energy of SiF quoted by Gaydon is very much less than that predicted.

The rough general picture that emerges is that the properties of XY_4 and XY can be approximately predicted one from the other in terms of

" equilibrium-variation ", although the experimental data are incomplete, and although it would appear that a more refined theory is necessary to derive the force constants from the frequencies in XY_4.[87]

Considering the dihalides of tin, however, we might expect that the distances, force constants, and bond energies should be intermediate between those of SnHal and $SnHal_4$. Unfortunately, the force constants in $SnHal_2$ are not known ; but the distances in the dihalides are *larger* than in the tetrahalides, while the bond energies are *larger* (15, 14 kcal. : see Section II) instead of being *smaller* as one might expect. It is clear therefore that we cannot explain the differences between these molecules entirely in terms of equilibrium-variation.

To sum up : (*a*) Pauling's remarkable empirical generalisations are strongly supported by the experimental evidence, chosen as it has been to avoid difficulties due to uncertain heats of vaporisation. (*b*) The empirical value of the concept of " thermal electronegativity " is discussed, and a simple extension suggested which may prove of value in discussing bond energies for given atoms in *different* valency states. The Schomaker–Stevenson rule is shown to break down for the halides of carbon, but (*c*) this can be roughly accounted for in terms of a simple theory of " non-bonding " repulsion which, based on Lennard-Jones's work on virial coefficients, also agrees with Pauling's empirical " van der Waals radii ". (*d*) Some examples are given of the way in which third-law methods make more precise many important values for heats of reaction. (*e*) A comparison of evidence leads to the unexpected conclusion that the mono- and tetra-halides and -hydrides of these elements are closely related energetically, while the dihalides of tin (at any rate) are anomalous.

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[87] Cf. Torkington, *Trans. Faraday Soc.*, 1951, **47**, 105.

Note to Table 11.—*Diatomics.* All data for *r* and *k* are from Herzberg [18] except for CF, which is from Andrews and Barrow (*Proc. Phys. Soc.*, 1951, **64,** 481) ; all data for $_1B$ from Gaydon [17] except for the monohalides of Pb from Wieland and Newburgh (*Helv. Phys. Acta,* 1949, **22,** 590) and for CF from Andrews and Barrow (*loc. cit.*) *Polyatomics.* $_4r$ from Allen and Sutton,[19] *k* for S.V.F.F. from Herzberg, " Infra-Red and Raman Spectra of Polyatomic Molecules ", van Nostrand Co. Inc., New York, 1945 ; Heath and Linnett.[82] Bond energies, see Section II and the vaporisation heats of Si, Ge, and Sn deduced in Section III ; the vaporisation heat of Pb and the dissociation energies of Cl_2, Br_2, and I_2 are from Bichowsky and Rossini ; [21a] that of F_2 has been taken as 39 kcal./mole (Doescher, *J. Chem. Physics*, 1952, **20,** 330). Two values of $_4B$ are given for carbon corresponding to $L = 170$, 125 kcal./g.-atom ; for PbF_4 we have used Q_f (solid) 222 kcal./mole (v. Wartenberg, *Z. anorg. Chem.*, 1940, **240,** 337), and estimated the vaporisation heat from the boiling point.

TABLE 11. *Comparisons of data for* XY, XY_4, *and* XY_2

	Diatomic XY				Pentatomic XY_4					Triatomic XY_2	
	$_1r$, Å	k, 10^5 dyne/cm	$_1B$	$_1B$, calc.	$_4r$, Å	k, 10^5 dyne/cm.			$_4B$, kcal /mole	$_2r$, Å	$_2B$
			kcal /mole			S.V.F.F	Heath and Linnett	Calc.			
CH . . .	1·120	4·45	80	92 or 82	1·093	5·04	$\simeq$ S.V.F.F.	5·05	99 or 88	—	—
CF . . .	1·271	7·17	$\sim$ 114	111 or 101	1·36	9·14	4·32	(8·14)	120 or 109	—	—
CCl . . .	—	3·77	—	72 or 62	1·765	4·38	1·79	(4·28)	78 or 67	—	—
CBr . . .	—		—	61 or 51	1·94	3·36	1·38	—	66 or 55	—	—
CI . . .	—		—		2·15	—	—	—	—	—	—
SiH . . .	1·520	2·46	—	70	—	2·84	$\simeq$ S.V.F.F.	2·79	76	—	—
SiF . . .	1·603	4·90	88 ± 9	122	1·54	7·16	5·7	5·56	132	—	—
SiCl . . .	—	2·63	76 ± 11	81	2·02	3·75	2·55	2·99	87	—	—
SiBr . . .	—	2·20	69 ± 11	65	2·15	2·92	2·01	2·50	70	—	—
SiI . . .	—	—	—	48	2·43	—	—	—	52	—	—
GeH . . .	—	—	—	—	—	—	—	—	—	—	—
GeF . . .	—	3·92	—	97	1·67	—	—	4·45	105	—	—
GeCl . . .	—	2·31	62 ± 9	61	2·08	3·27	2·40	2·62	66	—	—
GeBr . . .	—	1·96	58 ± 9	47	2·29	2·58	1·90	2·22	51	—	—
GeI . . .	—	—	—		2·50	—	—	—	—	—	—
SnH . . .	1·785	1·46	< 74	—	—	—	—	1·66	—	—	—
SnF . . .	—	3·28	76 ± 11	—	—	—	—	3·72	—	—	—
SnCl . . .	—	1·98	74 ± 11	69	2·30	2·80	2·34	2·25	74	2·42	89
SnBr . . .	—	1·71	46 ± 23	57	2·44	2·28	1·84	1·94	62	2·55	76
SnI . . .	—	—	—	—	2·64	—	—	—	—	2·73	63
PbH . . .	1·839	1·43	—	—	—	—	—	1·62	—	—	—
PbF . . .	—	2·63	80	76	—	—	—	2·99	82	—	—
PbCl . . .	—	1·63	72	—	2·43	—	—	1·85	—	2·46	72
PbBr . . .	—	1·45	69	—	—	—	—	1·65	—	2·60	53
PbI . . .	—	1.19	65	—	—	—	—	1·35	—	2·79	44