317. *The Dissociation Energy of Fluorine.**

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The objections raised by some authors to von Wartenberg's evaluation of $D(F_2)$ = 63·5 kcals. g.-mol.$^{-1}$ appear to be well founded. Recent work by Schmitz and Schumacher and by Wahrhaftig appears to be much more reliable. It is concluded that the experimental data *at present available* as a whole indicate strongly a value for $D(F_2)$ of about 37 kcals. g.-mol.$^{-1}$, certainly not greater than about 45 kcals. g.-mol.$^{-1}$.

The energy terms which enter into the calculation of electron affinities using the Born–Haber cycle have been re-examined. It is considered that a value of $D(F_2)$ = 37 kcals. g.-mol.$^{-1}$ leads inescapably to a value for the electron affinity of *gaseous* fluorine atoms which is less than that of chlorine. There appear to be no uncertainties in the various energy terms which could be large enough to reverse this conclusion. On the other hand, it has been shown that the electron affinity of fluorine in solution (*i.e.*, the electron affinity of the gaseous atom plus the heat of solution of the negative ion) remains larger than that of chlorine. The effects of changes in the value for $D(F_2)$ on the heats of a number of simple processes of interest and on the ionic character of covalent bonds involving fluorine have been discussed.

Published work leads mainly to two widely different values for the dissociation energy of the fluorine molecule. The spectroscopic studies on fluorine by von Wartenberg, Sprenger, and Taylor (1), and by Bodenstein, Jockusch, and Sing Hou Chong (2) are considered to indicate a value for $D(F_2)$ of about 64 kcals. per g.-mol. On the other hand, more recent spectroscopic and thermochemical work on the ClF molecule by Wahrhaftig (3) and by Schmitz and Schumacher (4) lead to a much lower value, in the neighbourhood of 33 kcals. Very recently Barrow and Caunt (5) have published the results of spectroscopic work with RbF and CsF and have concluded that their observations lead to a value for $D(F_2)$ of about 50 kcals.

There have been few published attempts to assess the reliability of the different claims and it seemed to us that such a survey would be useful, particularly since a number of other important energy quantities, such as the electron affinity of the fluorine atom and certain bond energies, are dependent on the value of $D(F_2)$.

The Spectrum of Fluorine.—The estimate of $D(F_2)$ = 63·3 kcals. by von Wartenberg, Sprenger, and Taylor (1) was based on the following considerations. The absorption spectrum of fluorine is entirely continuous, whereas the spectra of the remaining halogens show both a continuum and a band system. Thus $D(F_2)$ cannot be estimated by a band-convergence method. Von Wartenberg, Sprenger, and Taylor listed, for all four halogens, the values then available for λ_m, the wave-lengths at which the continuum shows a maximum absorption. In the cases of Cl_2, Br_2, and I_2 they also listed the available values for λ_c, the convergence limit of the band system. A plot of $\lambda_c - \lambda_m$ against atomic number gave a straight line. Extrapolation of this line gave a value of $\lambda_c - \lambda_m$ for fluorine from which λ_c and hence $D(F_2)$ were derived.

These authors pointed out that this method had no theoretical basis. Such a straight line requires the existence of extremely special relations between the potential energy curves of the ground and the excited states for the series of molecules, Cl_2, Br_2, and I_2. It is difficult to see why such a connection should exist. Mulliken (6) has also criticised both the data and the theoretical basis of this method.

There are two other high values for $D(F_2)$ in the literature. The value of 70 kcals. deduced by Bodenstein *et al.* (2) is not an observation; it is based merely on an interpolation from a smooth curve of $D(X_2)$ against the atomic number of X for the series H_2, Cl_2, Br_2, and I_2. From a study of the long-wave-length continua of LiF, NaF, and KF, Desai (7) deduced a value of 72 kcals. for $D(F_2)$. Gaydon (8) has pointed out that this estimate is worthless since it is based on old thermochemical data now known to be incorrect. Using recent thermochemical data, Gaydon found that Desai's spectroscopic results lead to $D(F_2)$ = 24, 48, and 62 kcals. from LiF, NaF,

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* Based on a paper read at the Symposium on " Fluorine Chemistry " on November 30th, 1949.

and KF, respectively. Very little can be concluded from such scattered results, except perhaps that $D(F_2)$ is not as high as von Wartenberg's value.

The Thermochemistry and Spectrum of ClF.—The first observations in serious conflict with $D(F_2) = 63{\cdot}3$ kcals. were provided by Wahrhaftig's work (3) on the absorption spectrum of ClF. He observed 13 bands with a good convergence limit and found that $D(ClF) = 60{\cdot}3$ kcals., on the assumption that dissociation to excited fluorine atoms occurs. If $Q_f(ClF)_g$ is the heat of formation of gaseous ClF from the elements in their standard states,* we have

$$Q_f(ClF)_g - D(ClF) + \tfrac{1}{2}D(Cl_2) + \tfrac{1}{2}D(F_2) = 0 \qquad \ldots\ldots \quad (1)$$

The values of the dissociation energies refer to absolute zero whereas the heats of formation refer to room temperature. However, the correction is negligible compared to the uncertainties in some of the data used.

If $D(Cl_2) = 57{\cdot}1$ kcals. (8) and $D(ClF) = 60{\cdot}3$ kcals. (3),

then $$D(F_2) = 63{\cdot}4 - 2Q_f(ClF)_g \text{ kcals.}$$

At the time of the appearance of Wahrhaftig's paper, two values of $Q_f(ClF)_g$ were available from thermochemical experiments, *viz.*, 27·4 (9) and >22 kcals. (10) These values give $D(F_2) = 8{\cdot}6$ and $<19{\cdot}4$ kcals., respectively.

Gaydon (8) has drawn attention to another feature which he considers indicates a value of $D(F_2)$ less than 63·3 kcals. Data are available for the first five vibrational levels of the ground state of HF. (11) The usual Birge–Sponer plot shows a marked positive curvature and hence it would be expected that $D(HF)$ would lie *below* the value of 138 kcals. obtained by a linear extrapolation. Gaydon points out that the values of $D(F_2)$ and $D(HF)$ are linked thermochemically by the value of $Q_f(HF)_g$. $D(F_2) = 63{\cdot}3$ kcals. leads to $D(HF) = 147$ kcals., a value *higher* than the linear extrapolation value.

The spectroscopic and thermochemical work of Schmitz and Schumacher (4) provides the strongest evidence for a value of $D(F_2)$ much lower than 63·3 kcals. These authors repeated Wahrhaftig's work (3) on the absorption spectrum of ClF. The ClF was prepared in two ways: (*a*) directly from pure Cl_2 and F_2, and (*b*) by mixing ClF_3 and Cl_2 in the correct proportions in the absorption cell at 350°. The two samples gave the same spectrum. The absorption measurements were carried out at room temperature and 1·5 atmospheres pressure, thus ensuring that the transitions to the upper electronic state originated almost entirely from the zeroth vibrational level of the ground state. It seems very unlikely that there can be much error in the assessment of the convergence limit in this case since transitions were observed to 14 vibrational levels of the upper state, which possesses a very shallow hollow in the potential-energy curve.

Schmitz and Schumacher used three different extrapolation methods, which give a maximum divergence of 0·8 kcals. in the value for D'_0, the dissociation energy of this upper state (5·0—5·8 kcals.). Wahrhaftig (3) gives 8·0 kcals. for this quantity, but it is unlikely that the uncertainty in the convergence limit itself is as large as the difference between these estimates of D'_0. The value of D''_0, the dissociation energy of the ground state, is uncertain because it is not known which of the dissociation products is in an excited state. However, this uncertainty is not large since both atomic excitation energies are small (F 1·1, and Cl 2·5 kcals.).

Schmitz and Schumacher's work thus yields a range of values for D''_0 depending on the mode of extrapolation and the assumption concerning the atomic excitation. The values range from 58·4 to 60·7 kcals. Wahrhaftig's data yield the values 58·9 or 60·3 kcals. respectively, depending on whether an excited chlorine or fluorine atom is produced. Hence a value of $D(ClF) = 59{\cdot}6 \pm 1{\cdot}2$ kcals. can be open to very little uncertainty.

Schmitz and Schumacher also measured $Q_f(ClF)_g$, so that $D(F_2)$ could be evaluated from the equation given above. $Q_f(ClF)_g$ was obtained by measuring the heats of the following two reactions:

$$(NaCl)_c + \tfrac{1}{2}F_2 \longrightarrow (NaF)_c + \tfrac{1}{2}Cl_2 \qquad Q_1 = 39{\cdot}5 \pm 0{\cdot}5 \text{ kcals.}$$
$$(NaCl)_c + ClF \longrightarrow (NaF)_c + Cl_2 \qquad Q_2 = 24{\cdot}5 \pm 0{\cdot}1 \text{ kcals.}$$

The figure for Q_1 included a correction for a small quantity of ClF_3 which was formed. The Q_2 value was the mean of ten experiments. Von Wartenberg and Fitzner (12) had previously measured Q_1 and obtained $39{\cdot}3 \pm 0{\cdot}1$ kcals., a result in very close agreement with the above. Another, quite independent, estimate of Q_1 can be made from the Q_f values of $(NaCl)_c$ and $(NaF)_c$. It is clear that $Q_1 = Q_f(NaF)_c - Q_f(NaCl)_c$. The Q_f values given by Rossini and Bichowski (13) (which have each been obtained by indirect methods involving heats of solution

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* Q will be used throughout to indicate heats of formation from the elements in their standard states.

and neutralisation, etc.) give $Q_1 = 37{\cdot}7$ kcals. These three estimates seem to establish $Q_1 = 38{\cdot}7 \pm 1{\cdot}0$ kcals. with a considerable degree of certainty.

A second evaluation of Q_2 may be made in the following way. Schmitz and Schumacher (4) have determined the heat of the reaction :

$$\mathrm{ClF} + \mathrm{F_2} \longrightarrow \mathrm{ClF_3} \qquad Q_3 = 25 \pm 2 \text{ kcals.}$$

from the temperature dependence of the equilibrium constant. They also measured directly the heat of the reaction :

$$3(\mathrm{NaCl})_c + \mathrm{ClF_3} \longrightarrow 3(\mathrm{NaF})_c + 2\mathrm{Cl_2} \qquad Q_4 = 76{\cdot}5 \text{ kcals.} \quad \text{(No accuracy limits given)}$$

We have thus $Q_2 = Q_4 + Q_3 - 2Q_1 = 24{\cdot}1 \pm {\sim}4$ kcals.

Wicke and Schäfer (14) have independently determined Q_3 from the temperature dependence of the equilibrium constant. Their value is $Q_3 = 26{\cdot}5 \pm 0{\cdot}5$ kcals. Combining this with Q_1 and Q_4 we obtain $Q_2 = 25{\cdot}6 \pm {\sim}2{\cdot}5$ kcals. These latter estimates of Q_2 add considerable support to the figure obtained by the direct determination. However, they involve data from experiments which Schmitz and Schumacher state to be less accurate than the direct determinations of Q_1 and Q_2. Accordingly the evaluation of $Q_f(\mathrm{ClF})_g = Q_1 - Q_2$ has been carried out by using $Q_2 = 24{\cdot}5 \pm 0{\cdot}1$ kcals. and the above average value of $Q_1 = 38{\cdot}7 \pm 1{\cdot}0$ kcals. This gives $Q_f(\mathrm{ClF})_g = 14{\cdot}2 \pm 1{\cdot}1$ kcals. Wicke (15) has recently measured directly the heat of formation of ClF from the elements. By pressure measurements he has shown that, under the conditions of his experiments, no $\mathrm{ClF_3}$ was formed. He obtained $Q_f(\mathrm{ClF})_g = 11{\cdot}6 \pm 0{\cdot}4$ kcals. Combining this with the above value to cover the whole range of uncertainty gives $Q_f(\mathrm{ClF})_g = 13{\cdot}3 \pm 2{\cdot}1$ kcals.

Introducing this value into equation (1), together with $D(\mathrm{ClF}) = 59{\cdot}6 \pm 1{\cdot}2$ and $D(\mathrm{Cl_2}) = 57{\cdot}1$ kcals., gives :

$$D(\mathrm{F_2}) = 36{\cdot}4 \pm 7{\cdot}6 \text{ kcals.}$$

Table I summarises the data used in deriving this figure for $D(\mathrm{F_2})$.

TABLE I.

$$\begin{array}{rcll}
(\mathrm{NaCl})_c + \tfrac{1}{2}\mathrm{F_2} & \longrightarrow & (\mathrm{NaF})_c + \tfrac{1}{2}\mathrm{Cl_2} & Q_1 \\
(\mathrm{NaCl})_c + \mathrm{ClF} & \longrightarrow & (\mathrm{NaF})_c + \mathrm{Cl_2} & Q_2 \\
\mathrm{ClF} + \mathrm{F_2} & \longrightarrow & \mathrm{ClF_3} & Q_3 \\
3(\mathrm{NaCl})_c + \mathrm{ClF_3} & \longrightarrow & 3(\mathrm{NaF})_c + 2\mathrm{Cl_2} & Q_4
\end{array}$$

Q_1	Method.
$39{\cdot}3 \pm 0{\cdot}1$	Direct, v. W. and F. (12)
$39{\cdot}5 \pm 0{\cdot}5$	Direct, S. and S. (4)
$37{\cdot}7$	Indirect, R. and B. (13)

Q_1 chosen $= 38{\cdot}7 \pm 1{\cdot}0$ kcals.

Q_2	Method.
$24{\cdot}5 \pm 0{\cdot}1$	Direct, S. and S. (4)
$24{\cdot}1 \pm {\sim}\ 4$	From Q_3 (4) and Q_4 (4)
$25{\cdot}6 \pm {\sim}\ 2{\cdot}5$	From Q_3 (4) and Q_4 (14)

Q_2 chosen $= 24{\cdot}5 \pm 0{\cdot}1$ kcals.

$Q_f(\mathrm{ClF})_g = Q_1 - Q_2 = 14{\cdot}2 \pm 1{\cdot}1$ kcals.
$Q_f(\mathrm{ClF})_g = 11{\cdot}6 \pm 0{\cdot}4$ kcals., Wicke (15).
$Q_f(\mathrm{ClF})_g$ chosen $= 13{\cdot}3 \pm 2{\cdot}1$ kcals.
$D(\mathrm{ClF})$ chosen $= 59{\cdot}6 \pm 1{\cdot}2$ kcals.

$$D(\mathrm{F_2}) = 36{\cdot}4 \pm 7{\cdot}6 \text{ kcals.}$$

This range of values includes all the uncertainties in the various quantities used. It does not include the older estimates of $Q_f(\mathrm{ClF})_g$, *viz.*, 27·4 (9) and >22 kcals. (10). Inclusion of these figures would give a result for $D(\mathrm{F_2})$ *lower* than the above value with a wider range of uncertainty.

We consider that the figure which we have chosen for the heat of formation of $(\mathrm{ClF})_g$ cannot be seriously in error. The number of independent observations involved is fairly considerable and forms a convincing body of data. Likewise the value chosen for $D(\mathrm{ClF})$ seems to be open to little uncertainty, unless the *interpretation* of the spectrum of this molecule is seriously in error. Wicke (16) has suggested that this is, indeed, the case. He give the following argument.

If Morse curves are constructed for the upper and lower states of the chlorine molecule, using the known constants, a fairly good estimate can be obtained for the frequency of the intensity maximum in the continuous spectrum. This is obtained, using the Franck–Condon principle, by finding the point at which a vertical line, drawn from the minimum of the lower-state potential-energy curve, cuts the repulsion side of the Morse curve for the upper state. The estimated $h\nu_{\max.}$ is less than the observed value by less than 10 kcals., in terms of energy. Wicke points out that the same procedure applied to the case of ClF, using the constants given by Wahrhaftig (3), gives a calculated value for $h\nu_{\max.}$ about 40 kcals. lower than the experimental value reported by Schmitz and Schumacher (4). Wicke, therefore, concludes that considerable doubt attaches to the figure $D(\mathrm{ClF}) \approx 60$ kcals. which has been obtained from this spectrum.

Wicke's conclusion appears to us by no means sure. It is well known that a Morse curve is merely an approximation, even in the region below the dissociation limit. Above this limit the Morse curve will be an even more uncertain approximation, and this, we feel, will be particularly exaggerated for curves which possess very shallow minima. We do not consider, therefore, that a poor result for a particular example of this type of calculation, which is concerned with features of the continuous spectrum, impairs the conclusions drawn from the band convergence which lies in quite a different region of the spectrum. It is difficult to envisage a more plausible interpretation of these bands than the one which has been suggested by the original observers.

Recently Barrow and Caunt (5) have measured the heats of dissociation of gaseous RbF and CsF. $D(F_2)$ may be estimated from these observations, since

$$\tfrac{1}{2}D(F_2) = D(\mathrm{MF}) + L(\mathrm{MF}) - L(\mathrm{M}) + Q_f(\mathrm{MF})$$

where $D(\mathrm{MF})$ = the dissociation energy of the alkali-metal fluoride to normal atoms, $L(\mathrm{MF})$ = the heat of sublimation of the fluoride, $Q_f(\mathrm{MF})$ = the heat of formation of the fluoride, and $L(\mathrm{M})$ = the heat of sublimation of the alkali metal, all these quantities referring to 18°.

In this way Barrow and Caunt arrive at the figure $D(F_2) = 50 \pm 6$ kcals., the two fluorides giving results in close agreement. Although little uncertainty attaches to the $Q_f(\mathrm{MF})$ and $L(\mathrm{M})$ values, this is not so for $L(\mathrm{MF})$, for which the correction to 18° requires an extrapolation over an extremely wide temperature range ($>1000°$). It is not improbable that in this way a considerable error of the same sign and nearly the same magnitude for the two fluorides can enter into the calculations. Barrow and Caunt point out that the greatest uncertainty lies in this $L(\mathrm{MF})$ term and they conclude that a precise value for $D(F_2)$ cannot be obtained in this way, until accurate values for $L(\mathrm{MF})$ are available. Caunt and Barrow (17) have also used a similar cycle involving thallous fluoride and arrived at the result $D(F_2) \leqslant 45$ kcals.

When the *available experimental* data are considered as a whole it is clear that an accurate value for $D(F_2)$ which can be accepted with confidence is not yet available. However, we are of the opinion that on the basis of the existing experimental data and the interpretation of these data the value of $D(F_2)$ must lie somewhere in the range :

$$D(F_2) = 37 \pm 8 \text{ kcals. per g.-mol.}$$

SOME CONSEQUENCES OF A CHANGE IN THE VALUE FOR $D(F_2)$.

The Thermal Dissociation of F_2.—Wicke (15) has objected to the value of ~33 kcals. for $D(F_2)$ suggested by Schmitz and Schumacher (4). He has pointed out that this low value would demand an appreciable degree of dissociation of fluorine molecules at ~1000°. In a recent paper (16) he has described some thermal conductivity experiments from which he concludes that the percentage dissociation of fluorine is negligible up to 1000° and that $D(F_2)$ cannot lie in the range 30—40 kcals.

Wicke's experiments consisted of a comparison of the thermal conductivities of F_2 and N_2 over a temperature range of 100—1000°, a nickel wire coated with nickel fluoride being used. Within an experimental error of ±10% the thermal conductivities of F_2 and N_2 were found to be the same. Hence Wicke concluded that fluorine is not appreciably dissociated even at 1000°.

Clearly, the main difficulty in experiments of this kind is to prevent attack of the nickel wire during the measurements. This is accentuated, in this case, by the extreme reactivity of fluorine. The attack, even if not sufficiently rapid to destroy the wire quickly, would introduce an exothermic heat term which would tend to mask the effect produced by dissociation. In using this method to distinguish between dissociation energy values it is the measurements in the higher regions of temperature which are clearly of the greatest importance. Such temperature regions, however, involve the greatest likelihood of attack on the wire. From the details given in Wicke's paper, we are not convinced that in this important temperature range attack on the wire by the fluorine is definitely excluded.

The nickel wire was coated by previous exposure to fluorine at red heat (presumably ~700°). There is no evidence presented which shows that this attack by fluorine definitely comes to an end, *i.e.*, that the coating completely protects the wire from further slow attack. Also, the wire was used for measurements at temperatures up to 300° ***higher*** than that use for the coating process. Further, Wicke states that above 1000° the wire " burnt through." This is certainly due to attack by fluorine since the melting point of nickel is ~1450°. The strongest indication that this coated nickel wire was unreliable is that Wicke could not obtain satisfactory results with it in experiments with bromine at high temperatures. It is stated that the nickel wire, both uncoated and coated with nickel fluoride, was not stable. Only by using a platinum wire at 800° in the same apparatus was the thermal conductivity observed which corresponded to the expected degree of dissociation.

Wicke and Schäfer (14) have carried out similar thermal conductivity measurements with ClF_3 using a nickel wire. They have obtained values of the equilibrium constant for $ClF_3 \rightleftharpoons ClF + F_2$ which are in agreement with those obtained by other methods. We have already referred to their estimate of the heat of this reaction. However, it is important to note that in these latter experiments the temperature of the wire did *not exceed* 460°. The possibility of attack of the wire is clearly very much less in this case.

We have calculated the equilibrium constant K_c and the percentage dissociation for $F_2 \rightleftharpoons F + F$ at various temperatures and two widely different initial fluorine pressures. The following well-known expression has been used :

$$K_c = \frac{(C_F)^2}{(C_{F_2})} = \frac{\frac{1}{N_0}\left[\frac{(2\pi m\boldsymbol{k}T)^{3/2}}{\boldsymbol{h}^3}\right]^2 \sigma_{F_2} v_F{}^2 \boldsymbol{h}^2}{\frac{(2\pi \, . \, 2m\boldsymbol{k}T)^{3/2}}{\boldsymbol{h}^3} \, . \, v_{F_2} 8\pi^2 A\boldsymbol{k}T \, . \, \mathrm{f}(v)_{F_2}} \, . \, e^{-E/\boldsymbol{R}T}$$

in which C_F and C_{F_2} are concentrations in moles c.c.$^{-1}$, m = the mass of the fluorine atom in g., $\boldsymbol{k}$ = Boltzman's constant, $\boldsymbol{h}$ = Planck's constant, T = absolute temperature. σ_{F_2} = the symmetry number of F_2 (= 2), v_F = the electronic partition function for fluorine atoms, v_{F_2} = the electronic partition function for F_2 (= 1), A = the moment of inertia of F_2, E = the dissociation energy of the fluorine molecule, and $\mathrm{f}(v)_{F_2}$ = the vibrational partition function of F_2.

The fundamental frequency of vibration, ν_0, of F_2 in the expression $\mathrm{f}(v)_{F_2} = \left[1 - e^{-\frac{h\nu_0}{kT}}\right]^{-1}$, is not known.* We have estimated it by assuming that the restoring force constant for F_2 is the same as that for I_2. In the above expression for K_c, two different values of E, *viz.*, 37 and 45 kcals. have been used; the latter corresponds to the highest value of $D(F_2)$ which we consider possible. The results are given in Table II; P_{F_2} is the initial pressure of fluorine.

TABLE II.

	E = 37 kcals.			E = 45 kcals.		
		P_{F_2} = 380 mm.	$P_{F_2} = 10^{-2}$ mm.		P_{F_2} = 380 mm.	$P_{F_2} = 10^{-2}$ mm.
Absolute temperature.	K_c.	Dissociation, %.		K_c.	Dissociation, %.	
1273	$5{\cdot}11 \times 10^{-6}$	40	100	$2{\cdot}19 \times 10^{-7}$	10·2	100
1073	$3{\cdot}39 \times 10^{-7}$	11·5	100	$0{\cdot}82 \times 10^{-8}$	1·9	93·5
873	$6{\cdot}37 \times 10^{-9}$	1·5	90·5	$0{\cdot}66 \times 10^{-10}$	—	25·7

The values of the percentage dissociation given in Table II indicate that it might be possible to make a direct determination of $D(F_2)$ by measuring the temperature coefficient of the equilibrium constant for $F_2 \rightleftharpoons 2F$. Under certain conditions the dissociation is very marked and should be easily measurable, apart, of course, from serious technical difficulties arising from the great reactivity of fluorine.

Bond Dissociation Energies of the Halogens and of Molecules isoelectronic with Fluorine.—The old value of $D(F_2)$ = 63·5 kcals. leads to a monotonous decrease in the dissociation energy of the halogen molecules along the series F_2 to I_2. Within the range of values 37 ± 8 kcals. this decrease no longer occurs; the dissociation energies show a maximum at chlorine. This feature, if it is established, might be understood in the following way. In Mulliken's terminology, the classification of the orbitals of the fourteen electrons, which derive from the outer *s* and *p* electrons of the two separate halogen atoms, is the same except for a progressive increase in principal quantum number from fluorine to iodine. The classification is

$$(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4$$

The $(z\sigma)^2$, $(x\sigma)^2$ and $(w\pi)^4$ electrons are bonding, and the $(y\sigma)^2$ and $(v\pi)^4$ electrons are anti-bonding. On this basis, a monotonous gradation in dissociation energy might be expected since the binding energy of the bonding electrons would decrease with increasing principal quantum number and increasing screening power of the inner shells. However, from Cl_2 to I_2 an additional

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* *Added in proof.* Since this paper was submitted for publication an experimental value for ν_0 has become available. This gives K_c values which are about 30% higher than those shown in Table II and, consequently, slightly larger values for the percentage dissociation.

factor can operate. There may be a certain degree of hybridization between *p* and *d* orbitals of the *same* principal quantum number in the case of the valence electrons of the separated atoms. This would increase the bonding power and decrease the anti-bonding power of these electrons. The degree of hybridisation would increase from Cl_2 to I_2, but, of course, in this sequence other factors supervene and cause an overall decrease in the bond energy from Cl_2 to I_2. In fluorine, however, a different situation may well arise because the atom possesses no *d* orbitals of the same principal quantum number and hence there can be no hybridisation offsetting the anti-bonding power of the *p* electrons.

We have also considered the possibility of understanding this maximum in the bond energies of this series in terms of resonance between covalent and ionic structures, *viz.*, X : X and X^+X^-. The energy of separation between the covalent and the ionic structures will be markedly larger for F_2 than for the rest of the halogens, on account of the extremely high ionisation potential of fluorine. Thus a sequence of increasing values of the ionic resonance energy, together with a sequence of decreasing pure covalent-bond energies, might result in a maximum binding energy at chlorine. However, it is found that this demands a value for the resonance energy in the case of chlorine which is improbably large.

There is another trend of bond dissociation energies which is of some interest, *viz.*, that in the sequence along the first row of the Periodic Table. The data are :

Molecule	C_2H_6	N_2H_4	H_2O_2	F_2
Bond	C–C	N–N	O–O	F–F
Dissociation energy, kcals.	86 [a]	60 ± 3 [b]	53·6 [c]	37 ± 8 (63·5)

[a] Taken from the Table given by Steacie, " Atomic and Free Radical Reactions," New York, 1946. [b] Szwarc, *Proc. Roy. Soc.*, 1949, *A*, **198**, 267. [c] From $Q_f(H_2O_2)$ and $D(O–H) = 101$ kcals.; Gaydon (8).

It is seen that, with our suggested range for $D(F_2)$, the above trend is monotonous, whereas this is not the case if $D(F_2) = 63·5$ kcals. We feel that this steady decrease in dissociation energy is of more significance that the sequence $F_2 \longrightarrow I_2$, since, as we have already indicated, there are grounds for the belief that the $F_2 \longrightarrow I_2$ trend should not necessarily be monotonous.

The thermochemistry of reactions involving fluorine. A change of $\Delta D(F_2)$ in the value for the dissociation energy of fluorine will produce a change of $\frac{1}{2}\Delta D(F_2)$ per F atom in Q_a, the heat of formation of a fluoride from gaseous atoms. Hence, estimates from heats of formation of the dissociation energies of single bonds to fluorine atoms will be altered by $\frac{1}{2}\Delta D(F_2)$; *e.g.*,

$$D(R–F) = Q_a(R–F) - Q_a(R)$$

This change of $\frac{1}{2}\Delta D(F_2)$ also applies to estimates of " average bond energies " or " bond energy terms " in a polyatomic molecule. On the other hand, Q_f values for fluorides, *i.e.*, heats of formation of the compounds from the elements *in their standard states*, are clearly independent of $D(F_2)$. There are various simple processes of interest, the heats of which are independent of changes in $D(F_2)$:

(1) $F_2(g) + H_2(g) \longrightarrow 2HF(g)$

(2) $RH + F_2 \longrightarrow RF + HF$

(3) $R_1·CH_2·CH_2·F \longrightarrow R_1·CH{:}CH_2 + HF$

(4) $e^- + RF \longrightarrow R + F^-$

A change of $\Delta D(F_2)$ in $D(F_2)$ produces a change of $\frac{1}{2}\Delta D(F_2)$ in $D(RF)$ and, as will be seen from a later section of this paper, an exactly offsetting change in E_F, the electron affinity of a gaseous fluorine atom.

(5) The sodium " flame " reaction,

$$(Na)_g + (RF)_g \longrightarrow (Na^+F^-)_g + R·_g$$

In contrast to the above examples, in a reaction system which contains fluorine molecules any considerations concerning the possible rôle played by the dissociation $F_2 \longrightarrow 2F$ will be affected by the value of $D(F_2)$ adopted. Also the heats of reactions of the type,

$$F_2 + A \longrightarrow F + F–A$$

in which A is a molecule or radical, will be altered by $\frac{1}{2}\Delta D(F_2)$. Examples of interest are :

$$H + F_2 \longrightarrow HF + F$$
$$R· + F_2 \longrightarrow RF + F$$
$$F_2 + CH_2{:}CHR \longrightarrow F·CH_2·CHR– + F$$

A striking consequence of our conclusion that $D(\mathrm{F}_2) < 45$ kcals. is that the value of the electron affinity of a gaseous fluorine atom, derived by means of the Born–Haber cycle, is not greater than, and probably *less* than, that of chlorine. This is discussed fully in the next section.

The Electron Affinity of Fluorine.—For an alkali-metal halide MX, the Born–Haber cycle leads to the expression:

$$E_x = Q(\mathrm{MX})_c + S(\mathrm{M})_c + I(\mathrm{M}) + \tfrac{1}{2}D(\mathrm{X}_2) + U_0$$

in which E_x = the electron affinity of the gaseous halogen atom, $Q(\mathrm{MX})_c$ = the heat of formation of crystalline MX from $(\mathrm{M})_c$ and *gaseous* X_2, $S(\mathrm{M})_c$ = the heat of sublimation of the alkali metal, $I(\mathrm{M})$ = the ionisation potential of the alkali-metal atom, $D(\mathrm{X}_2)$ = the dissociation energy of the halogen molecule, and U_0 = the lattice energy of crystalline MX.

Using this method, Sherman (18) found the following electron affinity values:

F, 98·5; Cl, 92·5; Br, 87·1; I, 79·2.

Mayer and Helmholtz (19), using a different form for the ionic interaction energy, found:

F, 95·3; Cl, 86·5; Br, 81·5; I, 74·2.

Both these values for E_F are based on $D(\mathrm{F}_2) = 63·5$ kcals. It is clear that values of $D(\mathrm{F}_2)$ in the range 37 ± 8 would reduce the above figures by 13·2 ± 4 kcals., to values which are less than the corresponding chlorine figures. This consequence has already been pointed out by Wicke (15), who uses it as an argument against a low value of $D(\mathrm{F}_2)$. We do not consider the argument acceptable. We have first examined the data used in the cycle to see if there are any uncertainties which may be sufficiently large to permit the conclusion that E_F could be greater than E_Cl, even with a low value for $D(\mathrm{F}_2)$ in the range suggested above.

Table III [taken from Rice (20)] is a typical presentation of the data used in the calculation of electron affinities. The lattice energies are the values obtained by Huggins (21), who has carried out the most comprehensive calculations of these quantities, corrected to room temperature. The remaining data are taken from Rossini and Bichowski (13). We have used our suggested range for the quantity $D(\mathrm{F}_2)$.

The most striking feature of Table III is the relatively small variation in the different E_x

TABLE III.

Salt.	$Q(\mathrm{MX})_c$.	$S(\mathrm{M})_c$.	$I(\mathrm{M})$.	$\tfrac{1}{2}D(\mathrm{X}_2)$.	$-U_0$.	E_x.	Average E_x.	E_x (exptl.).
LiF	145·6	39·0	123·8	18·5 ± 4	245·1	81·8 ± 4		
NaF	136·0	25·9	118·0	,,	216·4	82·0 ± 4		
KF	134·5	19·8	99·7	,,	193·2	79·3 ± 4	81·7 ± 4	
RbF	133·2	18·9	95·9	,,	183·4	83·1 ± 4		
CsF	131·7	18·8	89·4	,,	175·9	82·5 ± 4		
LiCl	97·6	39·0	123·8	28·9	201·1	88·2		86·6 [a], 92·7 [b]
NaCl ...	98·3	25·9	118·0	28·9	184·0	87·1		85·8 [c], 85·5 [d]
KCl	104·4	19·8	99·7	28·9	168·3	84·5	87·3	87·1 [d]
RbCl ...	105·1	18·9	95·9	28·9	162·1	86·7		
CsCl	106·3	18·8	89·4	28·9	153·2	90·2		
LiBr	87·6	39·0	123·8	23·1	189·9	83·6		86·5 [e]
NaBr ...	90·6	25·9	118·0	23·1	175·9	81·7		87·5 ± 4·6 [f]
KBr	97·9	19·8	99·7	23·1	161·5	79·0	81·8	88 ± 3·4 [g]
RbBr ...	99·6	18·9	95·9	23·1	156·1	81·4		80·5 ± 0·4 [h]
CsBr ...	101·5	18·8	89·4	23·1	149·6	83·2		83·9 [d]
LiI	72·5	39·0	123·8	18·1	176·2	77·2		74·6 [i], 72·4 [j]
NaI	76·7	25·9	118·0	18·1	164·4	74·3		72·6 [k], 76·3 [l]
KI	86·3	19·8	99·7	18·1	152·5	71·4	74·3	
RbI	88·5	18·9	95·9	18·1	147·9	73·5		
CsI	91·4	18·8	89·4	18·1	142·4	75·3		

[a] Saha and Tandon, *Proc. Nat. Inst. Sci. India*, 1937, **3**, 287, 296. [b] Mayer and Mitchell, *J. Chem. Physics*, 1940, **8**, 85, 282. [c] Mayer and McCallum, *ibid.*, 1943, **11**, 56. [d] Ionov, *Compt. rend. Acad. Sci. U.S.S.R.*, 1940, **28**, 512. [e] Piccardi, *Atti R. Accad. Lincei*, [vi], 1926, **3**, 566. [f] Blewett, *Physical Rev.*, 1936, **49**, 900. [g] Glockler and Calvin, *J. Chem. Physics*, 1936, **4**, 492. [h] Doty and Mayer, *ibid.*, 1944, **12**, 323. [i] Glockler and Calvin, *ibid.*, 1935, **3**, 771. [j] Mayer and Sutton, *ibid.*, p. 20. [k] *Idem*, *ibid.*, 1934, **2**, 146. [l] Ionov, *J. Exp. Theor. Phys. U.S.S.R.*, 1940, **10**, 1248.

values for a given halogen, and for Cl, Br, and I the satisfactory agreement between the mean of the calculated and experimental values. This indicates that, if there are any uncertainties in the data, they cannot be haphazard experimental errors but must have very special regularities and more or less cancel out in the case of the Cl, Br, and I cycles. Also in order to offset the decrease in E_F due to the lower value of $D(F_2)$, the errors should combine in such a way that the revised E_F values, derived from the different alkali-metal cases, are in reasonable agreement. For example, the complete neglect of any covalent character in the binding energy of the lattice might be considered to introduce errors.

The quantities I(M) and S(M) are open to little error, particularly the former. Moreover, the agreement in the five calculated values of E_x for each halogen demands that any errors in one or both of the terms I(M) and S(M) would have to be *the same for each alkali metal.* This can be ruled out. Similar considerations apply to Q_f(MX) for each alkali-metal halide. Further, it should be noted that von Wartenberg (12) and Schmitz and Schumacher (4) have independently determined $Q_f(\text{NaF})_c - Q_f(\text{NaCl})_c$ by a direct method, obtaining results in good agreement with the difference in the values given in Table III, which have been obtained separately by indirect methods. It seems extremely unlikely that this agreement would be obtained if there were any relatively large errors in the Q_f values for alkali-metal fluorides and chlorides.

There remains for consideration the lattice energy term. We have compared the calculated values of lattice energies from the following sources: Sherman (18), Mayer and Helmholtz (19), Huggins (21), Verwey and de Boer (22), Rice (20), and Slater (23). The underlying principles are the same in all cases but the methods vary in the details of the expressions used for the potential energy of the ionic crystals. In spite of such differences, the calculated values agree remarkably well amongst themselves and with the experimental values available. The largest divergence is about 5% in the worst cases but most of the deviations are less than this. What is more important for our considerations of E_F relative to E_{Cl} is that the variations in $U_0(\text{MF}) - U_0(\text{MCl})$, with the different methods, are still less—on the average 2 kcals., and never greater than 3 kcals.

This agreement in calculated values for lattice energies can be understood from the following simplified considerations. There are two widely used expressions for the potential energy of a crystal lattice in terms of attraction- and repulsion-energy terms. Simple forms of these are:

$$U_0 = -\frac{A\varepsilon^2}{r_0}\left(1 - \frac{1}{n}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$U_0 = -\frac{A\varepsilon^2}{r_0}\left(1 - \frac{\rho}{r_0}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which A is the Madelung constant, r_0 is the equilibrium interionic distance between nearest neighbours, and n and ρ are constants.

The constants n and ρ may be evaluated by relating $\mathrm{d}^2U_r/\mathrm{d}V^2$ to the compressibility of the crystal. In equations (2) and (3), the magnitudes of n and ρ are such that the second term is relatively small, so that the calculated values of U_0 are very insensitive to changes in the values of n and ρ. It can be seen that the methods of calculation of U_0 are all self-compensatory in the sense that, if an extra term is added to the potential-energy expression (*e.g.*, a van der Waals attraction term), then the use of the condition $(\mathrm{d}U/\mathrm{d}V)_{r_0} = 0$ and the evaluation of n and ρ from the relation between $\mathrm{d}^2U/\mathrm{d}V^2$ and the compressibility will compensate for this new term, through an inevitable change in the repulsion term. The critical parameter in these calculations is r_0, and the values of this are known very accurately for the alkali-metal halides. We are of the opinion that, unless the generally accepted principles underlying lattice-energy calculations are abandoned for a completely new approach, any serious revision of U_0 values, particularly of the kind which would render $E_F > E_{Cl}$, is very unlikely.

We consider that this examination of the Born–Haber cycle leads inescapably to the conclusion that if $D(F_2)$ lies in the range 37 ± 8 kcals., the electron affinity of a gaseous fluorine atom cannot be greater than, and is very probably less than, that for chlorine.

The Electron Affinity of Fluorine in Aqueous Solution.—The work of M. G. Evans and his collaborators (24) on oxidation–reduction reactions has emphasised the importance of a quantity which may be termed the solution electron affinity of a radical. This quantity is the sum of the electron affinity of the gaseous atom or radical and the heat of solution of the corresponding negative ion, *i.e.*, $E + H_s$. The difference between $E + H_s$ values for two radicals may be very different from the difference between the electron affinities of the gaseous radicals. For example $E_{Cl} - E_{OH} \approx 40$ kcals., whereas $(E + H_s)_{Cl} - (E + H_s)_{OH} \approx 3$ kcals. It is of some interest to examine the situation with regard to fluorine. Differences in $(E + H_s)$ values can be derived from the equations:

$$M_c + \tfrac{1}{2}(X_2)_s \longrightarrow M^+_\infty + X^-_\infty \quad . \quad . \quad . \quad . \quad Q_f(MX)_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$M_c + \tfrac{1}{2}(Y_2)_s \longrightarrow M^+_\infty + Y^-_\infty \quad . \quad . \quad . \quad . \quad Q_f(MY)_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\tfrac{1}{2}(Y_2)_s \longrightarrow (Y)_g \quad . \quad . \quad . \quad . \quad . \quad . \quad \tfrac{1}{2}Q_f(Y)_g \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$(X)_g \longrightarrow \tfrac{1}{2}(X_2)_s \quad . \quad . \quad . \quad . \quad . \quad . \quad -\tfrac{1}{2}Q_f(X)_g \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which M is an alkali metal, and X and Y are halogens, the suffix *s* denoting the halogen molecules in their *standard states*. Equation (4) − (5) + (6) + (7) gives:

$$(X)_g + Y^-_\infty \longrightarrow X^-_\infty + (Y)_g \quad . \quad . \quad . \quad [Q_f(MX)_\infty - \tfrac{1}{2}Q_f(X)_g] - [Q_f(MY)_\infty - \tfrac{1}{2}Q_f(Y)_g]$$

It is clear that the heat of this reaction is the difference in the $(E + H_s)$ values for the two halogens, *i.e.*, $\Delta(E + H_s)(X/Y)$. These differences have been calculated for the four halogens from the data given by Rossini and Bichowski (13) for the alkali-metal salts. The mean values are:

	F/Cl.	Cl/Br.	Br/I.
$\Delta(E + H_s)$	24·1—32·1	13·0	16·6

The F/Cl value is based on $D(F_2) = 37 \pm 8$ kcals. It is seen that $(E + H_s)_F > (E + H_s)_{Cl}$ in spite of the fact that $E_F < E_{Cl}$. This is clearly because the smaller fluorine ion has a much higher heat of solution than the chloride ion. $(H_s)_F - (H_s)_{Cl}$ is positive and larger in magnitude than $E_F - E_{Cl}$. To illustrate this we have calculated ΔH_s values for the pairs of halogen atoms. It can easily be shown that

$$H_s(X) - H_s(Y) = [U_0(MX)_c - L(MX)_c] - [U_0(MY)_c - L(MY)_c]$$

in which $L(MX)_c$ and $L(MY)_c$ are the heats of solution of the crystalline alkali-metal halides MX and MY. A table of U_0 and L values is given by Rice (20). Mean values of ΔH_s from the data for the alkali-metal halides are:

	F/Cl.	Cl/Br.	Br/I.
ΔH_s	33·8	7·4	9·3

$\Delta H_s(F/Cl)$ is seen to be more positive than $\Delta(E + H_s)(F/Cl)$.

The Ionic Character of Covalent Bonds involving Fluorine Atoms.—The concept of covalent bonds with partial ionic character, as developed by Pauling (25), is well known. In many cases it is useful to describe the bond between two centres, say A and F, in terms of resonance between two structures A:F, in which A and F are linked by a pure covalent bond, and A^+F^-, in which A and F are linked by a pure electrovalency. The alternative ionic structure A^-F^+ can usually be neglected from energy considerations. If ψ_c and ψ_i are the wave functions for the covalent and the ionic structures, respectively, then $a_c\psi_c + a_i\psi_i$ is an approximation for the wave function for the actual state of the molecule AF. The coefficients a_c and a_i have values which minimise the energy. The percentage ionic character of the bond A–F is usually defined as $100a_i^2$.

If, at the normal internuclear separation of the bond A–F, the potential energies of the actual state of the molecule, the pure covalent structure, and the ionic structure are V_a, V_c, and V_i, respectively, then it can be shown that

$$a_i^2 \approx \frac{R}{2R + S}$$

in which $R = (V_c - V_a)$ is the resonance energy relative to the pure covalent structure and $S = (V_i - V_c)$ is the energy of separation between the pure covalent and the pure ionic structures. The potential energies V_a, V_c, and V_i all refer to the zero corresponding to dissociation into normal atoms or radicals, $A + F$. If V_{ii} is the potential energy of the ionic structure relative to the zero $A^+ + F^-$, then $V_i = V_{ii} + I_A - E_F$, and $S = V_{ii} + I_A - E_F - V_c$.

Consider the effect of a change of $\Delta D(F_2)$ in the value for the dissociation of fluorine on the percentage ionic character of an A–F bond. If V_a, which is negative, is determined from heats of formation, then it becomes $V_a' = V_a - \tfrac{1}{2}\Delta D(F_2)$. Pauling has suggested the empirical arithmetic mean rule for evaluating V_c, *viz.*:

$$V_c = -\tfrac{1}{2}[D(A\text{–}A) + D(F\text{–}F)]$$

V_c is negative, whereas D(A–A) and D(F–F) are usually taken as positive. On this basis V_c becomes $V_c' = V_c - \tfrac{1}{2}\Delta D(F_2)$. We have shown above that this change of $\Delta D(F_2)$ alters the electron affinity of fluorine by $\frac{1}{2}\Delta D(F_2)$. Hence V_i becomes $V_i' = V_i - \frac{1}{2}\Delta D(F_2)$. Substituting the new values V_a', V_c' and V_i' in the expressions for R and S shows that the values of these quantities remain unaltered. Hence the percentage ionic character is unchanged. Previously, simple calculations of ionic character on the above lines using $D(F_2) = 63{\cdot}5$ kcals. had led to the view that the ionic resonance energy and ionic character of H–F and C–F bonds was larger than that of the corresponding bonds for the remaining halogens. This view requires no revision if $D(F_2)$, and consequently E_F, are altered.

Incidentally, it is of interest to note that the relatively large ionic character of C–F and H–F bonds is not due to the higher electron affinity of fluorine. It is mainly due to the internuclear separations of these bonds being smaller than those involving the other halogens. This factor gives rise to smaller values of S and larger negative values for the so-called resonance integral, and hence to larger values of R. If Pauling's geometric mean rule is adopted for the evaluation of V_c, then changing $D(F_2)$ by $\Delta D(F_2)$ alters V_c by an amount which is not exactly $\frac{1}{2}\Delta D(F_2)$. This causes slight changes in R, S, and a_i^2. However, these differences are too small to be of any significance.

We have concluded that the existing experimental data indicate strongly that the dissociation energy of fluorine and the electron affinity of a gaseous fluorine atom are less than the corresponding quantities for chlorine. This may, at first sight, appear surprising. It is, therefore, of interest to note that there is evidence which points to the existence of the same situation for oxygen and sulphur.

To illustrate this we have collected the relevant data in Table IV. Two sets of data are presented for sulphur, since there are two alternative values for $D(S_2)$. The column labelled H gives data based on $D(S_2) = 83$ kcals. [Herzberg] (26), that labelled G is based on $D(S_2) = 101$ kcals. [Gaydon] (8). Unfortunately, there is no experimental value for $D(H{-}S\cdot)$ for the HS· radical. This quantity is required for the evaluation of $Qf(HS\cdot)$, E_{HS}, and $D(S{-}S)$ in H_2S_2. The values for $D(H{-}S\cdot)$ given in the Table are based on the following considerations. $D(H{-}O\cdot) = 101$ kcals., which is well established, is about 9 kcals. less than the average O–H bond energy in H_2O, *i.e.*, $Q_a(H_2O)/2$. There is evidence that $D(\colon N{-}H)$ is about 6 kcals. less than $Q_a(NH_3)/3$. Since sulphur is even less electronegative than nitrogen we have concluded that the difference between $Q_a(H_2S)/2$ and $D(H{-}S\cdot)$ will be even less and have taken this difference to be about 3·5 kcals. The values of E_{HS} have been calculated from the lattice energies of NaHS and KHS given by West (27), who obtained a value for E_{HS} (61 kcals.) very close to those given in the table. The value of E_{OH} is the mean of values calculated from the lattice energies of the alkali-metal hydroxides given by Goubeau and Klemm (28). These authors give a mean value for E_{OH} of 48 kcals. The figures given for $D(S{-}S)$ in S_8 are obtained from $Q_a(S_8)_g/8$; we consider that the dissociation energy of one S–S bond in this ring will certainly be somewhat greater than these average values.

TABLE IV.

Sulphur.			Oxygen.	
Property.	Value.		Property.	Value
	H.	*G.*		
$Q_f(S)_g$	$-56{\cdot}1$	$-65{\cdot}1$	$Q_f(O)_g$	$-59{\cdot}1$
$D(H{-}S\cdot)$	78·9	83·4	$D(H{-}O\cdot)$	101
$Q_f(HS\cdot)$	$-29{\cdot}0$	$-33{\cdot}5$	$Q_f(HO\cdot)$	$-10{\cdot}0$
E_{HS}	59·3	63·8	E_{OH}	51·7 (40*)
$D(S{-}S)$ in H_2S_2	49·1	58·1	$D(O{-}O)$ in H_2O_2	53·6
$D(S{-}S)$ in S_8	$\geqslant 53{\cdot}4$	$\geqslant 62{\cdot}4$		

All energies are given in kcals.

* Value for E_{OH} derived by Baughan, Evans, and Polanyi (*Trans. Faraday Soc.*, 1941, **37**, 377).

It is seen that, independently of the uncertainty in $D(S_2)$, the electron affinity of the HS· radical is larger than that of the HO· radical. On the whole, the bond-energy data indicate that the dissociation energy of an S–S single bond is probably a little larger than that of an O–O single bond.

Thus it seems fairly conclusive that the surprising feature of the trends in dissociation energy and electron affinity in the halogen series which arises from the acceptance of a low value for $D(F_2)$ and have sometimes been regarded as evidence against such a value, is not, in fact, unique. Similar trends are shown by oxygen and sulphur.

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