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A Note on the Thermochemistry of Fluorine
and its Compounds

EXCLUDED FROM GENERAL DECLASSIFICATION SCHEDULE
EXECUTIVE ORDER 11652

N. W. Luft and L. A. Wiseman

with an Addendum by H.A. Skinner and H.D. Springall
of the University of Manchester, entitled,

Energy data on Thallium Fluoride and the Dissociation Energy of Fluorine

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Washington 25, D.C.

Att: ORDTM

1. References:

None.

2. Purpose of this Report:

Forwarded herewith as Inclosure 1 is E.R.D.E. (Explosives Research & Development Establishment) Report No. 6/M/49 (Technical Memo.) - "A Note on the Thermochemistry of Fluorine and its Compounds", by H.W. Luft and L.A. Wiseman, dated June 1949.

3. Abstract of Inclosure 1:

"The recent direct determinations of the energy of dissociation of ClF into atoms necessitates a new value for the energy of dissociation of the Fluorine Molecule. It is shown that the new value of $D(\text{F}_2) = 32.6 \text{ k.cals/mol.}$ is qualitatively supported by bond energies and bond distances in certain compounds and a possible reason for this very low energy is suggested. This new value leads to considerable changes in the value of $D(\text{HF})$ and the strength of the carbon-fluorine bond in CF_4 . Suggestions for further work to confirm this new value are made."

1 Incl: E.R.D.E. Tech Note. No. 6/M/49

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EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

E.R.D.E. TECHNICAL MEMORANDUM No. 6/M/49

A Note on the Thermochemistry of Fluorine and its Compounds

By

N.W. LUFT & L.A. WISEMAN

with an Addendum by

H.A. Skinner & H.D. Springall

of the University of Manchester,

entitled,

Energy data on Thallium Fluoride and the Dissociation
Energy of Fluorine.

This memorandum contains no information of overseas origin

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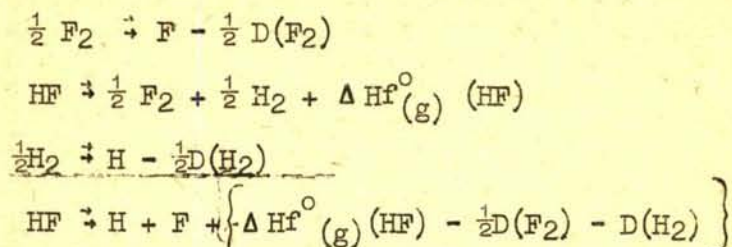
ABSTRACT

The recent direct determinations of the energy of dissociation of ClF into atoms necessitates a new value for the energy of dissociation of the Fluorine Molecule. It is shown that the new value of $D(\text{F}_2) = 32.6 \text{ k.cals/mol.}$ is qualitatively supported by bond energies and bond distances in certain compounds and a possible reason for this very low energy is suggested. This new value leads to considerable changes in the value of $D(\text{HF})$ and the strength of the carbon-fluorine bond in CF_4 . Suggestions for further work to confirm this new value are made.

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1. Introduction

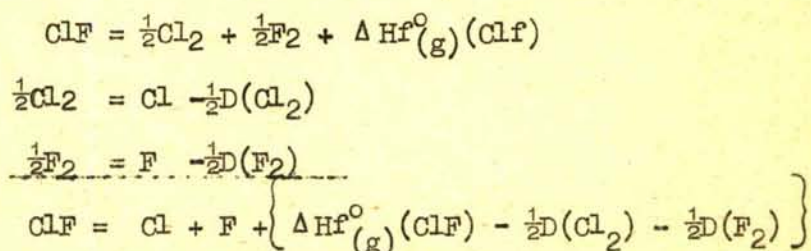
Whilst making an assessment of the use of Fluorine and its compounds in the field of rocket propellants, a brief survey of the thermochemistry of fluorine was undertaken. The previously accepted values are reasonably self-consistent as can be seen from the following:-



Thus $\text{D}(\text{HF}) = \frac{1}{2} \text{D}(\text{F}_2) + \frac{1}{2} \text{D}(\text{H}_2) - \Delta \text{Hf}^\circ_{(\text{g})} (\text{HF})$. (The sign conventions adopted are given in the appendix.

The previously accepted values (1) for these quantities are $\text{D}(\text{F}_2) = 64.5$ k.cals/mol $\text{D}(\text{H}_2) = 103.2$ k.cals/mol and $\Delta \text{Hf}^\circ_{(\text{g})} (\text{HF}) = -64.2$ k.cals/mol, (of which the value for $\text{D}(\text{H}_2)$ is quite certain), thus $\text{D}(\text{HF})$, calculated from the above equation, is 148 k.cals/mol. This value is a little higher than the value of 140 k.cal/mol obtained by a linear Birge-Sponer extrapolation of the vibrational levels of the ground state which is rather surprising (vide infra), but, since the bond in HF is not purely covalent, too much weight could not be placed on this extrapolation and the figure of 148 k.cals/mol. was accepted (e.g. Herzberg (2)).

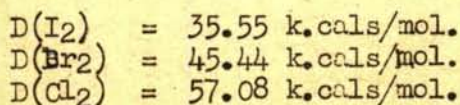
The value of $\text{D}(\text{ClF})$ can be obtained as follows:-



The value for $\text{D}(\text{Cl}_2)$ is 58.02 k.cals/mol. and the previously accepted value for $\Delta \text{Hf}^\circ_{(\text{g})} (\text{ClF})$, given by Ruff and Menzel (3), is -25.7 k.cals/mol. From these figures we get a value of $\text{D}(\text{ClF})$ of 87.0 k.cals/mol. Recently, however, new experimental values for $\text{D}(\text{ClF})$ of about 60 k.cals/mol. and for $\Delta \text{Hf}^\circ_{(\text{g})} (\text{ClF})$ of about -15 k.cals/mol. have been obtained and thus it is clear that a critical consideration of all this data must be undertaken.

2. The value of $\text{D}(\text{F}_2)$

The value accepted by Herzberg (2) for $\text{D}(\text{F}_2)$ is 2.8 e.V./mol. i.e. 64.5 k.cals/mol. The absorption spectra of Fluorine shows no banded structure and thus it is not possible to find $\text{D}(\text{F}_2)$ from a convergence limit. Wartenberg, Sprenger and Taylor (4) compared the wavelengths of the maxima in the absorption spectra of the halogens with the values for the energies of dissociation and obtained a value $\text{D}(\text{F}_2) = 63.3$. This method has no theoretical basis and the figure was accepted because it seemed to fit in with the D values (referred to 0°K) of the other halogens viz:-



/Bodenstein

Bodenstein, Jockusch and Shing Hou Chong (5) have repeated the work on the absorption spectra and have slightly modified the results of Wartenberg et alia (4) on the position of the absorption maximum of fluorine. A value of $D(F_2) = 70 \pm 1$ k.cals/mol. was obtained but again by an extrapolation which is theoretically unjustifiable.

Gaydon (6) refers to some measurements by Desai (7) in which the long wave absorption limits of LiF, NaF and KF were measured. These, when combined with recent thermochemical measurements, give values for $D(F_2)$ of 24, 48 and 62 k.cals/mol. respectively (Desai gave $D(F_2) = 76$ k.cals/mol. but this is based on discredited thermal data). Finally, Lederle (8) gives a value of $D(F_2) = 66.8$ k.cals/mol. from an extrapolation of electron affinity data.

It is clear that the previously accepted value of $D(F_2) = 64.5$ k.cals/mol. is not reliable; the work of Desai suggests the possibility of lower values.

3. The Heat of Formation of HF

The measurement of the heat of formation of HF is a reliable one, the early figures being due to Wartenberg and Fitzner (9) and Ruff and Laas (10). The thermal data must be corrected for the polymerisation of HF in the vapour phase (see Simons and Hildebrand (11). Ruff and Menzel (3) and Benesi and Smyth (12)) but this correction is small. Wartenberg and Schulza (13) have carried out measurements at 100°C and have obtained a value which is very close to the previous ones. Recently Wartenberg (14) has slightly modified this value and finds $\Delta H_f^0(g) = 64.5 \pm 0.2$ k.cals/mol. We shall take the values given in Ref. 1 viz:-

$$\Delta H_f^0(g) = -64.2 \text{ k.cals/mol.} \quad \text{Ref. 1 also gives } \Delta H_f^0(g) = -426.0 \text{ k.cals/mol. for } (HF)_6,$$

from which it can be seen that any corrections for polymerisation are small.

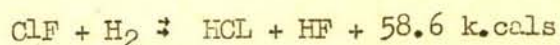
4. The value of $D(ClF)$

It was shown in the Introduction that, with the previously accepted values for $D(F_2)$, $D(Cl_2)$ and $\Delta H_f^0(g)(HF)$, the value of $D(ClF)$ was 87.0 k.cals/mol. Recently, however, the absorption spectrum of ClF has been examined and a band system found which exhibits a very clear convergence limit. Wahrhaftig (15) has obtained in this way the value $D(ClF) = 60.31$ k.cals/mol. and Schmitz and Schumacher (16), the value $D(ClF) = 60.3 \pm 0.5$ k.cal/mol. Both authors assume that dissociation produces an excited fluorine atom (in $2P_{1/2}$ state) with an excitation energy of 1.16 k.cals/atom. There may thus be some uncertainty as to the state of the atoms formed on dissociation but this cannot lead to an error greater than 1 or 2 k.cals/mol. We shall accept this value $D(ClF) = 60.3$ k.cals/mol. as does Gaydon (6).

5. The Heat of Formation of ClF

Fredenhagen and Krefft (17) estimated by a comparison of the heat evolved in the reactions between $Cl_2 + F_2$ and $H_2 + F_2$ that the heat of the former reaction was not less than 22 cal/mol. (i.e. $-\Delta H_f^0(g)(ClF) > 22$ k.cals/mol.).

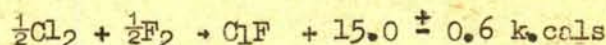
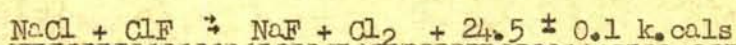
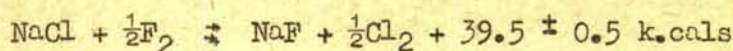
The reaction is certainly exothermic and often occurs explosively. Ruff and Laas (10) measured the heat evolved in the reaction



which gives a value of $\Delta H_f^0(g)(ClF) = -27.5$ k.cals/mol.

/Recently

Recently Schmitz and Schumacher (18) obtained a value of $\text{Hf}^0_{(g)}(\text{ClF}) = -15.0 \pm 0.6 \text{ k.cals/mol.}$ from the heat change in the following reactions:-



Wicke (19), in the course of a discussion on the bond energies of fluorine compounds, mentions that he has determined the value of $\Delta\text{H}^0_{(g)}(\text{ClF}) = -11.6 \pm 0.4 \text{ k.cals/mol.}$ by direct combination of the elements but does not give details.

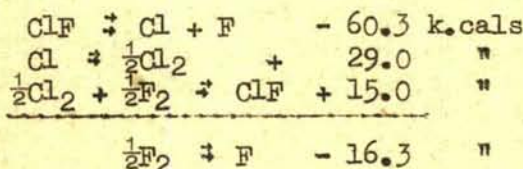
These recent values are quite incompatible with that of Ruff and Laas (10) ($\Delta\text{H}^0_{(g)}(\text{ClF}) = -27.5 \text{ k.cals/mol.}$) and favour a distinctly lower value for $\Delta\text{H}^0_{(g)}(\text{ClF})$. We shall therefore accept the value of $\Delta\text{H}^0_{(g)}(\text{ClF}) = -15.0 \pm 0.6 \text{ k.cals/mol.}$ although it has been stated (20) that the reaction between F_2 and NaCl is difficult to initiate and maintain.

6. Reconsideration of the value for $\text{D}(\text{F}_2)$ and $\text{D}(\text{HF})$

For the purpose of discussion we shall accept the following values viz:-

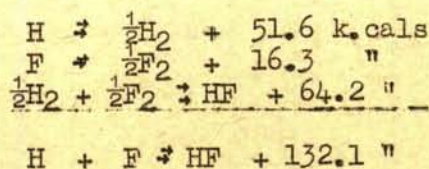
$\text{D}(\text{ClF})$	=	60.3	k.cals/mol.
$\Delta\text{H}^0_{(g)}(\text{ClF})$	=	15.0	" "
$\Delta\text{H}^0_{(g)}(\text{HF})$	=	64.2	" "
$\text{D}(\text{Cl}_2)$	=	57.2	" "
$\text{D}(\text{H}_2)$	=	103.2	" "

With these we can determine the value of $\text{D}(\text{F}_2)$ as follows:-



thus $\text{D}(\text{F}_2) = 32.6 \text{ k.cals/mol.}$ It should be noticed that the value of Ruff and Laas (10) of $\Delta\text{H}^0_{(g)}(\text{ClF}) = -27.5 \text{ k.cals/mol.}$ is quite impossible if we accept $\text{D}(\text{ClF}) = 60.3$ as then $\text{D}(\text{F}_2) = 7.6 \text{ k.cals/mol.}$ On the other hand a value of $-\Delta\text{H}^0_{(g)}(\text{ClF}) < 15 \text{ k.cals/mol.}$ is extremely unlikely as ClF is a stable, although very reactive compound, and its formation from its elements can be mildly explosive. We are thus led to the conclusion that if $\text{D}(\text{ClF}) = 60.3 \text{ k.cals/mol.}$ a low value for $\text{D}(\text{F}_2)$ must be accepted.

From the equations



we obtain a value of $\text{D}(\text{HF}) = 132.1 \text{ k.cals/mol.}$ Gaydon (6) has compared the spectroscopic values with the thermochemical values of $\text{D}(\text{HX})$, where X is a halogen. The spectroscopic values were obtained by a linear Birge-Sponer extrapolation and are compared with the thermochemical values

in the following Table. The thermochemical values were obtained from $\Delta H_f^\circ(g)$ (HX) (direct measurement) and $D(X_2)$ and $D(H_2)$ derived from reliable spectroscopic measurements.

TABLE I

Molecule	D (HX)	
	Thermochemical	Spectroscopic
HI	71.5	96.8
HBr	87.4	110.7
HCl	102.3	124.5
HF	148 (a)	138.3
	132 (b)	

(a) previously accepted value
(b) value preferred in this note

It will be noted that the spectroscopic values (linear Birge-Sponer extrapolation) are higher than the true values for HI, HBr and HCl. Surprisingly the old value for $D(HF) = 148$ k.cals/mol. was higher than the extrapolated figure. The value of $D(HF) = 132$ k.cals/mol thus brings HF into line with the other hydrogen halides. This is, unfortunately, not conclusive as, in some cases, the linear extrapolation gives values lower than the true ones (Ref.6.Ch.V) but it is indicative as, in general, the extrapolated are higher than the true values.

There is independent support for the lower value of $D(F_2)$ in the bond distances of certain bonds. Pauling (21) quotes $0.64\text{\AA}$ as the bond radius of covalent fluorine and this should lead to values of $1.28\text{\AA}$ for the F-F bond and $1.30\text{\AA}$ for the F-O bond. The values actually found are $1.435\text{\AA}$ for F-F (Ref.24) in F_2 , $1.41\text{\AA}$ for O-F in F_2O , and $1.42\text{\AA}$ for O-F in $FOONO_2$ (Ref.21.p.166). On the other hand the values for HF (calculated $0.94\text{\AA}$, measured $0.92\text{\AA}$) and ClF (calculated $1.65\text{\AA}$, measured $1.63\text{\AA}$) agree very well. Some figures for bond energies are given in Table II. So is the difference in bond energy between bonds with F and Cl.

TABLE II

H-F 132.1	F-F 32.6	C-F 88.0	N-F 53.9 (65.2)	O-F 42.85
H-Cl 102.7	F-Cl 60.3	C-Cl 66.5	N-Cl 38.4 (46.2)	O-Cl 49.3
$\Delta + 29.4$	$\Delta -27.7$	$\Delta + 21.5$	$\Delta + 15.5 (19.0)$	$\Delta -6.5$
	Cl-F 60.3	SiF 130.8	-	S-F 68.85
	Cl-Cl 58.0	SiCl 87.4	-	S-Cl 66.1
	$\Delta 2.3$	$\Delta + 43.4$		$\Delta + 2.75$

The values given in Table II agree with those of Pauling (21) and Skinner (26) when the Pauling-Skinner values are corrected for the new

/value

value of $D(F_2)$. The values for N-F and N-Cl in brackets are those preferred by Skinner. If we now compare these figures with the values of the bond radii given by Pauling (21. p.164), the results in the following table are obtained.

TABLE III

$\Delta-F, \Delta =$	H	F	O	N	C	Cl	S	Si
Bond radius	0.30	0.64	0.66	0.70	0.77	0.99	1.04	1.17
$\Delta = (\Delta-F) - (\Delta-Cl)$	+29.4	-27.7	-6.5	+15.5	+21.5	+2.3	+2.75	+43.4
r calc.)	.94	1.28	1.30	-	1.41	1.63	-	1.81
r exp.) ΔF	.92	1.435	1.42	-	1.36 ^x	1.63	-	1.54

^x in CF_4

In this Table, and the preceding one, Δ is the difference in bond energy between ΔF and ΔCl . With the exception of HF, it can be seen that the value of Δ increases with increase in the size of Δ (i.e. covalent bond radius) and that the larger Δ is the ^{larger is the} difference between the calculated and experimental bond distance. At first sight it might be imagined that fluorine would form stronger bonds than chlorine in corresponding compounds on account of its greater electronegativity. Pauling (21, p.225 et seq.) has discussed this question and shown that the greater electronegativity of fluorine might lead to greater double bond contribution with fluorine compounds than with chlorine compounds. The marked difference between the bond strengths of C-Cl and Si-Cl compared with C-F and Si-F is probably due to this cause. However, Walsh (25) has pointed out that, in bonds between small atoms, a large electronegativity in one of the atoms may lead to repulsion between the bonding electrons and other electron orbitals and it is suggested that this is the cause of the unexpectedly low bond strengths of F-F and F-O. These conclusions are also supported by the differences in calculated and measured bond distances. The fact that H-F has the expected high bond strength may be ascribed to the fact that there is no other electron orbital in the H atom to lead to a repulsive force which would reduce the bond strength. Thus consideration of bond distances and bond strength qualitatively supports the new low value of $D(F_2) = 32.6$ k.cals/mol.

There is one other indication of a low energy of dissociation of Fluorine. Stacey (30) makes the following statement, ".... under normal conditions of temperature and pressure, gaseous fluorine acts in the form of molecular fluorine but at higher temperatures and particularly when released from UF_6 , AgF_2 and CoF_3 , it reacts atomically...."

7. The Strength of the C-F Bond

Pauling (21) gives a value of 107 k.cals for the strength of the carbon-fluorine bond. This is based on a heat of sublimation of carbon of 124.3 k.cals/mol. and the value $D(F_2) = 63.5$ k.cals/mol. He shows that this agrees well with other thermochemical data. Skinner (26) gives a slightly different value of 103.75 k.cals/mol. The heat of formation of CF_4 , given in Ref.1, is $-\Delta H_f^0(g)(CF_4) = 162.5$ k.cals/mol. This, with the value of 124.3 k.cals/mol. for the heat of sublimation of carbon and the new value of $D(F_2) = 32.6$ k.cals/mol., leads to a value for the bond strength of C-F of 88.0 k.cals/mol. Further, from the value of $-\Delta H_f^0(g)(C_2F_6) = 240$ k.cals/mol. (1) and the value of the C-C bond, given

by Pauling (21) as 58.6 k.cals/mol. a value for the carbon-fluorine bond strength of 88.0 k.cals is obtained. Thus the values are consistent. There are, however, difficulties. Firstly the bond strength of the carbon-hydrogen bond is 87.3 k.cals (21) or 87.75 k.cals (26) which is almost the same value as that for C-F. CF_4 is said to be stable at temperatures of the order of 1000°C (22) whereas CH_4 breaks down into carbon and hydrogen at 1200°C (27). This, however, may not be a serious objection as, even if CF_4 were thermally dissociated at 1200°C , it would almost certainly be formed again on cooling, unless special precautions were taken e.g. pyrolysis in an atmosphere of hydrogen when HF would probably be formed. It is unlikely that CH_4 would be re-formed so easily. In any case, there is no direct correlation between thermochemical bond energies and the energies necessary to break bonds in polyatomic molecules.

The second difficulty is, however, more weighty. We have shown that the bond strength of C-F in C_2F_6 is 88.0 k.cals if the C-C bond strength is 58.6 k.cals. Brockway (23) has shown that the C-C bond distance in C_2F_6 is 1.45 Å as compared with that of 1.54 Å in C_2H_6 . This must mean that the C-C bond is much stronger in hexafluoroethane than in ethane. This seems probable in view of the well established greater thermal stability of fully fluorinated hydrocarbons in comparison with normal hydrocarbons but is incompatible with the heats of formation quoted above. It should be noted that the selection of another value for the heat of sublimation of carbon, e.g. 170 k.cals/gr. atom, will not alter this situation. In this case the bond energies become: C-H = 98.7 k.cals, C-F = 99.4 k.cals, C-C = 81 k.cals.

Wicke (19) has quoted a value for $-\Delta\text{Hf}^\circ_{(g)}(\text{C}^{\text{W}}_+) = 231 \pm 3$ k.cals/mol. This is stated to be unpublished work of v. Wartenberg but no details are given. This new value leads to a bond energy of 105.3 k.cals for the C-F bond which is, however, quite incompatible with the value of 240 k.cals/mol. for $-\Delta\text{Hf}^\circ_{(g)}(\text{C}_2\text{F}_6)$.

Thus, to sum up, the values for the heats of formation of CF_4 and C_2F_6 lead to a value for the strength of the C-F bond which may be acceptable but does not explain the considerable shortening of the C-C bond in C_2F_6 and the greater thermal stability of fluorinated hydrocarbons compared with normal hydrocarbons. A small increase in the value of $-\Delta\text{Hf}^\circ_{(g)}(\text{C}_2\text{F}_6)$ would be sufficient, however, to give a noteworthy increase in the C-C bond strength in C_2F_6 e.g. a value of $-\Delta\text{Hf}^\circ_{(g)}(\text{C}_2\text{F}_6) = 250$ k.cals/mol. would give a value for the C-C bond of 68.4 k.cals.

8. Recommendations

In the data so far discussed, it has been seen that the new value for $\text{D}(\text{F}_2)$ explains some old facts but leads to difficulties with the heat of formation of C_2F_6 . There is, however, one other difficulty. Fluorine vapour shows no band structure in the visible spectrum according to Gaydon (6), although bands have been reported by Allmand and Maddison (28). A dissociation energy of 32.6 k.cals/mol. corresponds to a wave-length of about 8,500 Å and therefore fluorine might have an absorption spectrum in the very near infra-red. This is a subject for experimental investigation.

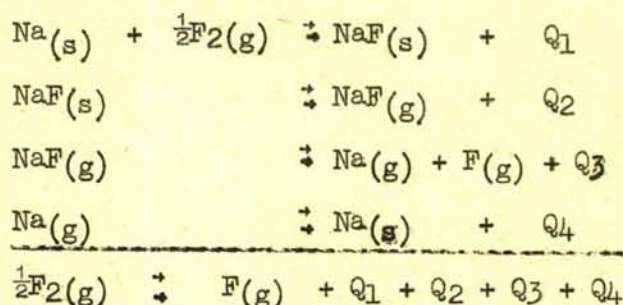
According to Bodenstein et alia (5) there is no thermal or photochemical reaction between hydrogen and fluorine in a magnesium vessel at room temperature. This vessel gave a very slow rate for the H_2/Cl_2 reaction and the authors believed that the walls of the magnesium vessel acted as very efficient chain breakers. They did observe reaction in a platinum vessel at -78°C and also a slight photochemical effect. These remarks are quoted from Noyes and Leighton (29). If the value of $\text{D}(\text{F}_2) = 32.6$ k.cals/mol. is correct, it might be possible to bring about the photochemical dissociation of F_2 with red light and this should have a marked effect on the H_2/F_2 reaction.

/It

It is possible to account for the non-appearance of an absorption spectrum in the very near infra-red if the first excited state of the F_2 molecule is either very much above the ground state, which is not considered very probable, or else is such that transitions from the ground state can only occur with much higher energies than 32.6 k.cals/mol. This would require a very steep repulsion curve, or one with a very shallow minimum, for the excited state. This is possible but it must be realised that the absence of absorption in the near infra-red would also imply that the H_2/F_2 reaction cannot be photochemically sensitised by light of such wavelengths.

It should be possible to measure experimentally the thermal dissociation of fluorine from pressure changes as a function of temperature in a closed system. (c.f. iodine). Admittedly, this is experimentally very difficult but it would give unambiguous evidence if thermal dissociation were observed.

Finally, it may be possible to get the value indirectly as suggested by Gaydon (6) e.g.



The data lacking are Q_2 and Q_3 . The measurement of Q_2 involves the measurement of the vapour pressure of $NaF(s)$. This can be done but there is some evidence that such molecules as $(NaF)_2$ may be formed which would lead to some ambiguity in interpretation (31). Q_3 could be determined spectroscopically e.g. atomic fluorescence.

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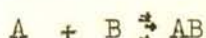
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APPENDIX

SIGN CONVENTIONS FOR THERMODYNAMIC QUANTITIES

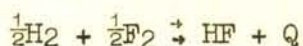
- (a) The heat of formation, ΔH_f° , is defined as the difference between the total heat content, H , of the products and that of the reactants in their "standard states" as defined by Lewis & Randall (32).



the heat of formation of the molecule AB is

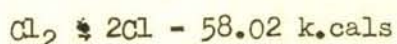
$$\Delta H_f^\circ(AB) = H_{AB} - (H_A + H_B)$$

It is clear from this that the heat of reaction Q , is equal to $-\Delta H_f^\circ$. Thus, the heat of formation of HF, $\Delta H_f^\circ(\text{HF})$, is equal to -64.2 k.cals/mol. but the heat evolved in the reaction



is $Q = +64.2$ k.cals/mol.

- (b) The heat of dissociation of the diatomic molecule A_2 , is written $D(A_2)$ and is the energy required to dissociate this molecule in its ground state into atoms in the ground state; thus $D(\text{Cl}_2) = 58.02$ k.cals/mol. at 300°K and the dissociation reaction can be written



- (c) The thermodynamic quantities refer to a reference temperature of 300°K .

S.89
M.232/49

ADDENDUM

SUMMARY

A study of the thermal and spectroscopic data on thallium fluoride leads to the evaluation of $D_0(F_2)$ as $\leq 32 \pm 10$ k.cals/mol.

INTRODUCTION

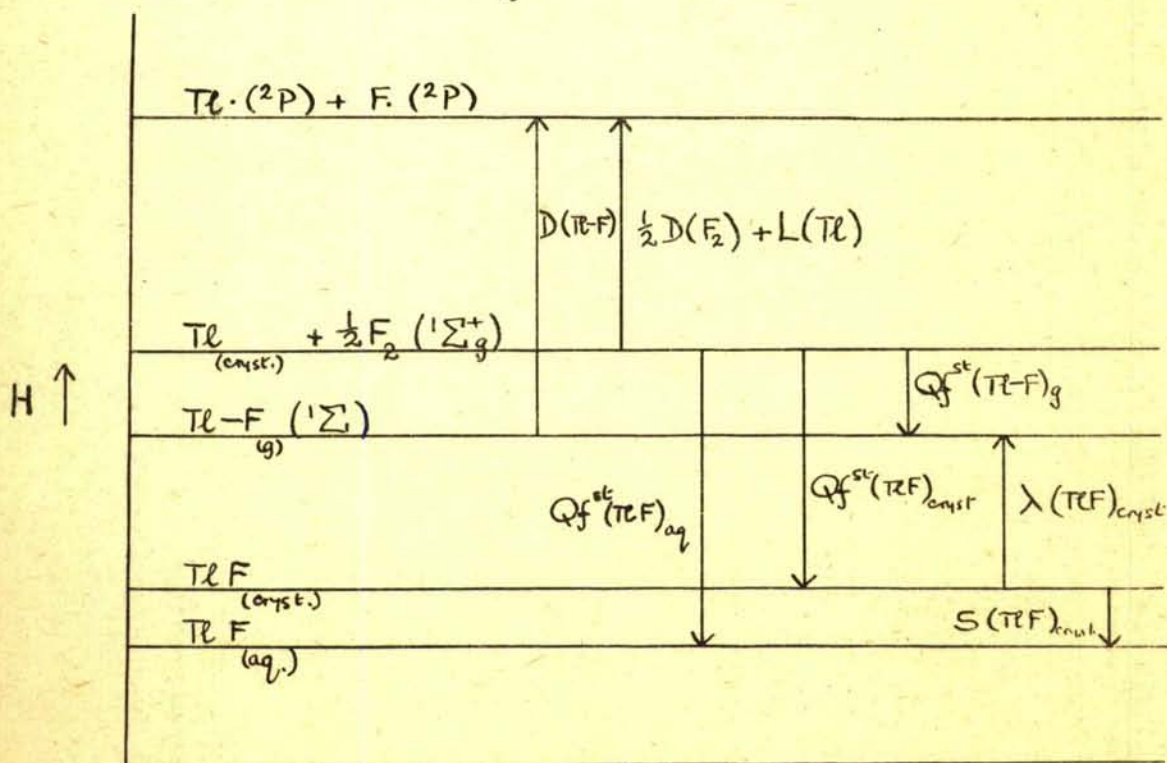
The problem of deciding between the two possible values for $D_0(F_2)^*$, (a) 2.8 eV (63.3 k.cals/mol) derived from intensity distribution in the F_2 continuum, and (b) ~ 1.4 eV (~ 33 k.cals/mol.) derived from recent spectroscopic and thermochemical data on ClF, has been considered in E.R.D.E. Tech. Memo. No. 6/M/49; the evidence appears to favour strongly the lower value.

Further evidence for $D(F_2) \sim 33$ k.cals/mol. can be obtained from spectroscopic and thermal data on thallium fluoride, TlF, by means of a simple thermochemical cycle.

Data on Thallium fluoride

The energy (H) levels of the TlF system involved are shown in Fig. 1.

Fig. I



* The dissociation energy, ΔH_0 , for $F_2 ({}^1\Sigma_g^+) \rightarrow 2F ({}^2P)$.

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The Q_f terms and the S term are $(-\Delta H)$ terms, heat liberated by the system reckoned positive; all the other terms are (ΔH) terms, heat absorbed by the system reckoned positive.

The simplest possible cycle based on these TlF energy levels gives

$$D(Tl-F)_g = \frac{1}{2}D(F_2) + L(Tl) + Q_f^{st}(Tl-F)_g$$

$$\text{i.e. } D(F_2) = 2 D(Tl-F)_g - L(Tl) - Q_f^{st}(Tl-F)_g$$

Now:

- (i) $D_o(Tl-F)$, the dissociation energy of $Tl-F$, ≤ 4.7 eV (108 k.cals/mol) (1,2)
- (ii) $L(Tl)$, the latent heat of sublimation of Tl_{metal} , = 40 k/atom. at 298°K (3)
- (iii) $Q_f^{st}(Tl-F)_g$, the heat of formation of gaseous $Tl-F$ from standard state elements, at 298°K, is not known. The closest approach to this term yet practicable comes from the expression

$$Q_f^{st}(Tl-F)_g = Q_f^{st}(TlF)_{aq} - S(TlF)_{cryst} - \lambda(TlF)_{cryst}$$

where

- (i) $Q_f^{st}(TlF)_{aq}$, the heat of formation of aqueous $(TlF \xrightarrow{M} TlF^{+800})$ = 77.5 k.cals/mol at 298°K,
- (ii) $S(TlF)_{cryst}$, the heat of solution of crystalline TlF in water has not been measured.

We are preparing thallium fluoride for a direct determination of $S^{800}(TlF)_{cryst}$. In the meantime an estimate of the value of this term can be obtained by analogy with the heats of solution of the other halides of thallium (3) and the halides of rubidium (4) and caesium (5), Table I, (the corresponding salts of thallium, rubidium and caesium show close resemblance in physical properties).

TABLE I

Heats of Solution (S) for MX

X	S for MX_{cryst} ($-\Delta H_{298}$, k.cals/mol.)		
	M = Rb	M = Cs	M = Tl
F	+ 5.9	+ 8.5	?
Cl	- 4.4	- 4.5	- 10.3
Br	- 5.9	- 6.6	- 13.7
I	- 6.5	- 8.1	- 17.7

It seems that $S(TlF)$ will be in the range 0 ± 5 k.cals/mol.

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(iii) $\lambda(\text{TlF})_{\text{cryst}}$, the heat of sublimation of crystalline
 TlF , = 25.1 kcal/mol at 298°K .

Conclusions

We have, thus, data of varying but assessable accuracy for the evaluation of $D(\text{F}_2)$ by the expression

$$D(\text{F}_2) = 2 \left\{ D(\text{Tl-F})_g - L(\text{Tl}) - Q_f^{\text{st}}(\text{TlF})_{\text{aq}} + S(\text{TlF})_{\text{cryst}} + \lambda(\text{TlF})_{\text{cryst}} \right\}$$

The combined errors in the evaluations of the L, S and λ terms are almost certainly within the range $\pm 10 \text{ kcal/mol}$. (There are small errors, negligible in comparison with those considered above, in the direct combination of $\pm \Delta H_{298}$ terms (L, Q_f , S and λ) with ΔH_0 terms (D)).

The TlF data therefore lead to

$$D_0(\text{F}_2) \leq 32 \pm 10 \text{ kcal/mol}.$$

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