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Hydrogen Fluoride and the Thermochemistry of Fluorine

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Hydrogen Fluoride and the Thermochemistry of Fluorine

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Hydrogen Fluoride and the Thermochemistry of Fluorine

George T. Armstrong

The thermochemistry of hydrogen fluoride is reviewed. The principal emphasis is on the experimental basis of the heats of formation of HF(g) and of HF(aq). Data from flame calorimetry in which HF(g) and HF(aq) are formed, evidence from processes involving other fluorine compounds, and some evidence from spectroscopic and photodissociation studies are brought together.

Key words: Fluorides; fluorine dissociation energy; fluorine thermochemistry; heats of formation; hydrofluoric acid; hydrogen fluoride.

I. Introduction

While it is possible for us to find certain unique features of most elements, in this note we wish only to examine some features of the element fluorine. We may list certain features which make it of special interest:

(1) It is a cornerstone element. With respect to the periodic system it is in the extreme upper right of the non-noble elements. As a result schemes that correlate properties within period or within group find that in both cases fluorine is the end element. Interpolation is rarely possible; - extrapolation is required in order to obtain properties by estimation.

(2) It is the most electronegative element and generally conceded to be the most reactive element. Thus bonds of unusual strength are formed to other elements; and most elements are found in compound with it (even some of the inert gases).

The chemistry and many physical properties of fluorine compounds are, therefore, frequently of interest as illustrations (paradigms) of these properties as found among all compounds. The thermochemistry of fluorine surely falls in this category.

The chemistry of fluorine showed a rather slow growth prior to World War II. The primary problems were related to its reactivity and to the need for proper materials for handling it. As a result of technological development during the war, however, this barrier was overcome, and the field of fluorine chemistry started very rapidly growing and became one of the most active fields in both organic and inorganic chemistry. This growth is symbolized in part by the formation of a division of fluorine chemistry in the American Chemical Society - one of the few divisions which is built around an element. Such great growth is probably due to the uniqueness of properties which fluroine compounds tend to display.

The thermochemistry of fluorine showed a parallel rapid growth with a number of laboratories setting up facilities for handling elemental fluorine as a reactant in the calorimetry; and others studying its thermochemistry, but limiting themselves to reactions involving only the combined element. We may refer to the Argonne National Laboratory; the Fulmer Research Institute in England, John Margrave's laboratory at Rice University; and the NBS laboratories, as examples of places where elemental fluorine could be handled. Both flow calorimetry and bomb calorimetry can be carried out in the NBS laboratories.

The use of reactions of fluorine compounds in which the element is never free has a longer history in calorimetry; and in fact the use of hydrofluoric acid solution calorimetry has played an important role in the thermochemistry of silcates and other mineral products for many years. However, application of bomb calorimetry to reactions involving aqueous HF has awaited the development of the rotating-bomb calorimeter.

Among the fluorine compounds there are many that have interesting features. There is one, however, that is almost omnipresent in the thermochemistry of fluorine - that is, hydrogen fluoride, either as the gas or as its aqueous solution, hydrofluoric acid. This compound has a complexity of its character, in particular the large degree of hydrogen bonding that it exhibits, which renders it a fit subject for investigation of many of its properties; but the feature which attracts our attention is its occurrence in so many reactions of fluorine compounds. For the chemistry of fluorine it has an importance analogous to the importance of water in the chemistry of oxygen.

In the thermochemistry of fluorine as in the chemistry of fluorine the acid or its aqueous solution occur in many processes that have been studied. As a result, the actual values that are derived for the heats of formation of various compounds are dependent on the value assigned to the heat of formation of hydrogen fluoride.[1]

A few examples are shown below of processes typical of those by which the thermochemistry of fluorine has been derived. These should be multiplied a hundredfold to give the true importance of the compound in this area.

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[1] In this note thermochemical values are given in kcal mol^{-1} as taken from the original literature or recent reviews in which the kcal is equivalent to 4184 J (exactly).

Typical Processes By Which the Thermochemistry of Fluorine Compounds Has Been Derived

(1) C_2F_4(solid polymer) + O_2(g) + $42H_2O$(1) = $2CO_2$(g) + $4[HF \cdot 10H_2O]$ (1)

(2) BeO(C) + 2HF(aq) = BeF_2(aq) + H_2O(1)

(3) NaF(c) = Na^+(aq) + F^-(aq)

(4) SiF_4(g) + $2H_2O$(g) = SiO_2(cristobalite) + 4HF(g)

We might ask ourselves the question: How precise and accurate do thermochemical values such as heats of formation have to be? This is a question that really has no exact answer. The answers depend upon the purposes to which the data are to be put.

We can give one answer which shows some inadequate values. See Table I.

Table I. Accuracy of Estimates of Heats of Formation of Some Fluorine Compounds

Compound	ΔH_f kcal mol^{-1} Estimate	Later Measurement	Error
NbF_5(c)	-342	-432	+90
PF_5(g)	-315	-381.4	+66
	-420		-39
RuF_5(c)	-300	-213.4	-87
SF_4(g)	-156	-171.7	+16
TaF_5(c)	-300	-455	+155
	-360		+95
		Average error	44 kcal mol^{-1}
		Average bias	26 kcal mol^{-1}

Estimates are selected from a review by Armstrong and Krieger [1].

In a recent review of the thermochemistry of fluorine compounds [1][*] we came across a number of compounds for which estimates of heat of formation had been made at a time there was no available measured value. The values that have been measured thereafter in some thirty cases were compared with the estimates. A sampling of the results, recently updated, is shown in Table I. The average error was 44 kcal mol^{-1}; the average bias was 26 kcal mol^{-1}. While it is not easy to say what is adequate accuracy; we would contend that this is not accurate enough for anything but the roughest work.

If one is trying to make equilibrium calculations, one should realize that an uncertainty of 1 kcal mol^{-1} in a heat of formation can lead, at room temperature, to an uncertainty of a factor more than 5 in its equilibrium concentration.

If one is trying to correlate bond lengths and strengths or determine changes in strain energies, a kilocalorie may be adequate for some cases, but for others a much smaller uncertainty is needed. If one is trying to carry out a Hess' law calculation that involves adding a number of reactions, one may want considerably better values.

We are dealing, in the case of hydrogen fluoride, with uncertainties of the order to 0.5 kcal mol^{-1}. To some who would be satisfied with the 1 or 2 kcal mol^{-1} our discussion may seem to be nitpicking. On the other hand, to those who are accustomed to the idea that the heat of formation of water has an uncertainty of about 0.01 kcal mol^{-1} this seems inadmissibly large.

II. Flame Calorimetry of Reactions Forming HF(g)

Several early calorimetric measurements of the energy of the reaction of the elements were used to arrive at the heat of formation of gaseous HF. A later reaction involving the combustion of ammonia suffers the same problems. These are shown in Table II.

There are two problems. The first is the problem of corrosion and accounting for all of the reaction products. The second which is a major one is the question of the non-ideality of gaseous HF has been the subject of several studies none of which is definative in the lower pressure region near room temperature. The gas undergoes polymerization, forming significant quantities of H_2F_2, H_3F_3, H_4F_4, H_6F_6, even at pressures of less than one atmosphere.

Figure 1 shows the quantity Z as a function of pressure along several isotherms. The quantity Z has the value 1 for an ideal gas. Note in the figure that it deviates from unity even at very low pressures.

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[*] Figures in brackets indicate the literature references on pages 14-16.

We are not prepared here to discuss all the PVT data, not all of which is shown here. Two or three sources but by no means all of them have been used in deriving the graph. It will be noted that the data from different sources are significantly different along several isotherms. Also of some importance is the fact that the data are incomplete at the very low pressure end, even though Z still deviates from unity. This lack of completeness has caused some difficulty in extrapolation. A model of the polymerization is necessary and the number of possible polymers renders the interpretation of such a model in the light of the available data somewhat ambiguous.

Figure 2 gives the parameter most interesting to us that can be derived from the PVT data, H°-H

Remembering that $H^\circ_{298} = H_{298} + (H^\circ_{298} - H_{298})$

we see from the figure that the enthalpy of the ideal gas differs from that of the real gas by several tenths of a kilocalorie per mole in this region. The solid lines represent values calculated from the work of Long, Hildebrand, and Morell [8]. The dashed lines represent the work of Strohmeier and Brieglib [9]. Note that these differ by a factor of two in this region. Medvedev [7] in 1963 made a recalculation of the correction for non-ideality based on the heat capacity of the real gas studied by Franck and Meyer [10] and of the ideal gas compiled by Gurevich, et al. [11]. This recalculation shows the non-ideality to be less again by a factor of two than we derived from the work of Breiglib and Strohmeier. In Table II we see several determinations of the heat of formation of HF and effects of corrections based on different interpretations of the non-ideality.

The value of -64.2 for NBS Circular 500 [12] was apparently derived by using the value of Ruff and Laas (as corrected by Ruff and Menzel) or by averaging three of the values shown.

If we refer to figure 2, we see in the inset that at higher temperatures the differences between various non-ideality corrections approach each other and tend to go to zero. Of the various measurements shown in Table II, only the one by von Wartenberg and Schutza was done at a high enough temperature that non-ideality corrections could be ignored. Thus this value is the only really unambiguous value for gaseous HF obtained by direct combination of the elements.

The measurement of the combustion of ammonia in fluorine suffers the same ambiguity as the other measurements.

The value -64.2 kcal mol^{-1} selected for NBS Circular 500 was generally accepted and received wide usage. An analysis of the heat of solution, some equilibrium constant data and heat of dilution data led to the heat of formation at a series of aqueous solutions. These values from Circular 500 are shown in Table III.

Table II

Flame Calorimetric Studies of the Heat of Formation of HF(g)

	ΔH°_f 298.15, kcal mol^{-1}		
$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) = HF(g)$	Original	Recalc(1)	Recalc(2)
Von Wartenberg and Fitzner (1926) [2]	-63.0	-63.8	-63.8
Russ and Laass (1929) [3]	-62.3	-64.2	-64.6
Von Wartenberg and Schutza (100°)(1932) [4]	-65.45	--	-64.41
$\frac{1}{3}NH_3(g) + \frac{1}{2}F_2(g) = HF(g) + 1/6\ N_2(g)$			
Armstrong and Jessup (1960) [5]	-64.22		-64.77
	-64.63		

Recalc(1) Ruff and Menzel (1931) [6]

Recalc(2) Medvedev (1963) [7]

Table III. Some Tabulated Values for $\Delta H_f[HF]$

	Ideal gas	10 H_2O	∞ H_2O
NBS Circular 500 [12]	-64.2	-75.605	-78.66
NBS Tech Note 270-3 [13]	-64.8	-76.235	-79.50
JANAF Tables [14]	-64.8±0.3		
Cox and Harrop [15]		-77.247*	-80.43*

*based on -64.8 for the ideal gas rather than -64.92 as used by Cox and Harrop.

III. Evidence Drawn from Other Reaction Processes

The first inkling the author had of a possible error in the heat of formation of HF came on examining the information collected in the middle and late nineteen fifties on the heat of formation of CF_4.

We may illustrate the nature of the clue by the following reactions:

Table IV.

$CH_4(g) + F_2(g) = 4HF(g) + CF_4(g)$

Jessup, McCoskey, and Nelson [16]
Using -64.2 kcal for $\Delta H_f[HF(g)]$ we get $\Delta H_f[CF_4(g)] = -220.4$

$$\begin{array}{ll} C_2F_4(\text{polymer}) + O_2(g) + 2H_2O(l) & = 2CO_2(g) + 4HF(aq\cdot 10H_2O) \\ \underline{C_2F_4(\text{polymer}) + O_2(g)} & \underline{= CO_2(g) + CF_4(g)} \\ CF_4(g) + 2H_2O(l) & = CO_2(g) + 4HF(aq\cdot 10H_2O) \qquad \Delta H = -41.5 \end{array}$$

Good, Scott, and Waddington [17]
Using -75.605 kcal for $\Delta H_f[HF\cdot 10H_2O]$ we get $\Delta H_f[CF_4(g)] = -218.3$

$C_2F_4(g) = CF_4(g) + C(c)$

$C_2F_4(g) + 2H_2(g) + 4[118.2\ H_2O]\ (l) = 2C(c) + 4[HF\cdot 118.2H_2O](l)$

$CF_4(g) + 2H_2(g) + 4[118.2\ H_2O]\ (l) = C + 4[HF\cdot 118.2H_2O](l)$

Neugebauer and Margrave [18]
Using NBS 500 value for $\Delta H_f[HF\cdot 118.2H_2O]$ we get
$\Delta H_f CF_4(g) = -217.5$

Note that CF_4 and HF appear on the same side in Jessup's reaction and on opposite sides in the other two.

We suggested that the above values could be reconciled if $\Delta H_f[HF]$ was in error by a few tenths of a kilocalorie per mole.

A number of other reactions were also available and tended to confirm this view.

One direction the above suggestion led was to a series of further determinations on $CF_4(g)$ and another direction was to a new appraisal of the heat of formation of HF(g) and HF(aq).

In every case, where the heat of formation of CF_4 and HF were tied together, the above suspicion was further confirmed. It became apparent at least to us, that so long as the uncertainty prevailed in the heat of formation of HF, no reaction involving both HF and CF_4 would be of much assistance in defining the heat of formation of CF_4. Other methods were sought and were brought successfully to a conclusion, we think.

With regard to the heat of formation of HF, a new series of studies was begun. The idea of trying to bring in the results of the relevant data obtained by the new techniques of fluorine bomb calorimetry was seriously proposed by Feder, Hubbard, Wise and Margrave [19]. They immediately derived a value of -64.92 kcal mol^{-1} for $\Delta H°F[HFg]$.

A typical series of reactions they introduced is shown in Table V.

Table V. A Series of Reactions Leading to $\Delta H_f[HF(g)]$ by Hess' Law

$$SiO_2(\alpha\text{-quartz}) + 2F_2(g) = SiF_4(g) + O_2(g) \qquad (1)$$

$\Delta H°_{298}(1) = -168.26 \pm 0.28$ [38]

$$SiO_2(\text{crystobalite}) = SiO_2(\alpha\text{-quartz}) \qquad (2)$$

$\Delta H°_{298}(2) = -0.35 \pm 0.05$ [39]

$$2H_2(g) + O_2(g) = 2H_2O(g) \qquad (3)$$

$\Delta H°_{298}(3) = -115.598 \pm 0.020$ [12]

$$SiF_4(g) + 2H_2O(g) = SiO_2(\text{crystobalite}) + 4HF(g) \qquad (4)$$

$\Delta H°_{298}(4) = +24.53 \pm 0.36$ [40,19]

$$2F_2(g) + 2H_2(g) = 4HF(g) \qquad (5)$$

$\Delta H°_{298}(5) = -259.676$

$\Delta H°_{f298}[HF(g)] = -64.92 \pm 0.12$

ΔH values are in kcal mol^{-1}, uncertainties are from [19], and are twice the standard deviations of the means.

The revised NBS values (for TN 270-3) by Evans and Parker [13] were prepared about this time and may have been influenced by this value.

There is available one completely different process for calculating the heat of formation of HF. This is the spectroscopic observation of the dissociation of HF.

Table VI. The Heat of Formation of HF(g)
From the Dissociation Energies of H_2, F_2, and HF

			$\Delta H^\circ_{298.15}$ kcal mol^{-1}	
H(g) + F(g)	=	HF(g)	-136.10	[20]
$\frac{1}{2}F_2$(g)	=	F(g)	+18.88	[13]
$\frac{1}{2}H_2$(g)	=	H(g)	+52.095	[13]
$\frac{1}{2}H_2$(g) + $\frac{1}{2}F_2$(g)	=	HF(g)	-65.125	

The necessary series of reactions is shown in Table VI. Note that the dissociation energy given by the work of Johns and Barrow [20] must be combined with the dissociation energy of fluorine. This may be the limiting step in the process. To illustrate the large amount of information available, we present in figure 3 the measurements uncovered in a review [1] of the work reported on this limited subject in a period of some 10 years following the issuance of NBS Circular 500. Distilled out of this mass of work, we find almost the only work upon which the current best value rests follows the analysis of Stamper and Barrow [21] (Figure 4), who obtained the dissociation energy from a 3rd law correlation of the experimental work of Wise [22] and of Doescher [23]. As you can see from the boundary lines, almost full weight was given to the work of Doescher. This has become a textbook example of the analysis of equilibrium data by the third law of thermodynamics. The figure, from Stamper and Barrow, was found in Pitzer and Brewer (Lewis and Randall) [24].

Note that the uncertainty (0.01 ev. or 0.23 kcal) assigned by the authors to the dissociation energy of HF would just about overlap the value currently accepted for HF (TN 270-3). In order for an error in the value assigned to the dissociation of F_2 to bring the ΔH_f into line would require a slightly larger dissociation energy of F_2 than we get from Stamper and Barrow's analysis.

IV. Recent Work on the Energy of Vaporization from Water

One of the more important contributions that came out following the revival of interest in HF was a series of reactions leading to the heat of solution of HF in H_2O by Cox and Harrop [15]. This threw a real monkey wrench into the situation. These reactions are found in Table VII.

The series of reactions was rather long, but each step was very small (except for the vaporization step). The series was planned in such a way as to allow no contribution from the non-ideality of the HF gas.

The value shown in Table III for $10H_2O$ was obtained from this sum of reactions, by merely adding to the heat of formation of HF(g) as listed for TN 270-3 [13].

The difficulty is that this is now a whole kilocalorie per mole more negative than had been selected for TN 270-3 which was already 0.63 or more kcal more negative than had been listed in NBS Circular 500 [12].

We have looked carefully over the work of Cox and Harrop for a source of discrepancy and so far certainly nothing positive has been discovered. We naturally turn to the largest term - the vapor pressure point. To get one kcal mol^{-1} by an error here would require the pressure to be in error by a factor of five, and even 0.4 kcal would require an error of a factor of two.

One tantalizing prospect is that there is an error in the calculation of ΔS for the reaction. Now S for HF(g) can be calculated quite accurately, and $S_{298}-S_0$ for LiF and $LiHF_2$ have both been measured in very reliable laboratories. If S_0 is zero for all substances, there hardly seems to be a chance for an error in calculating ΔS.

The possibility of a residual entropy for LiF seems hardly conceivable. The possibility of a residual zero point entropy for $LiHF_2$(c) seems not so far fetched - and this reminds us of the classical thermodynamic problems in the verification of the third law of thermodynamics.

Table VII. Cox and Harrop Study of HF(aq)

		ΔH°_{298} kcal mol^{-1}
(+)	$LiHF_2(c) + 6017\ H_2O(l) = [LiHF_2 \cdot 6017\ H_2O](l)$	1.860 ± 0.038[a]
(-)	$LiF(c) + 6008.67\ H_2O(l) = [LiF \cdot 6008.67\ H_2O](l)$	1.059 ± 0.028
(+)	$[HF \cdot 8.33\ H_2O](l) + 6008.67\ H_2O(l) = [HF \cdot 6017\ H_2O](l)$	-0.740 ± 0.006
(-)	$[HF \cdot 8.33\ H_2O](l) + [LiF \cdot 6008.67\ H_2O](l) = [LiHF_2 \cdot 6017\ H_2O](l)$	-0.177 ± 0.006
(-)	$LiHF_2(c) = LiF(c) + HF(g)$	13.410 ± 0.048
	$HF(g) + 6017\ H_2O(l) = [HF \cdot 6017\ H_2O](l)$	-13.172 ± 0.068

[a] Uncertainties are twice the standard deviation of the mean, assigned by Cox and Harrop.

We have here a very strong hydrogen bond (FHF^-). The question of the zero point entropy in salts containing the bifluoride ion has been the subject of numerous investigations. Westrum [25] did his thesis with Pitzer on this very subject (KHF_2) and satisfied himself by a thermodynamic cycle involving the heat capacity and vapor pressure of KHF_2 and the heat capacities of KF and HF that the proton is not assymetric. Other evidence is from structural analysis (neutron diffraction) (F-F distance) and from the infrared spectra of the salts. No positive evidence for an unsymmetrical hydrogen bond has been reported for KHF_2, KDF_2, $NaHF_2$. In the $H_2F_3^-$ ion the protons are assymetric as would be expected.

The evidence actually put forward on $LiHF_2$ is too limited to draw any conclusions specifically for it, the only direct evidence being a measurement of the F-F distance, which turns out to be only slightly greater than in KHF_2.

Table VIII. Vapor Pressure of HF Over $LiHF_2(c)$.

Effect of a Zero-Point Entropy of $LiHF_2(c)$

$LiHF_2(c) \rightarrow LiF(c) + HF(g) \quad P_{298} = 1.89 \pm 0.14$[a] Torr

$\Delta G^\circ = -RT \ln P = 3.553 \pm 0.044$ kcal mol^{-1}

$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$

with	S°_{298}	and assuming S°_0	or S°_0
	cal deg^{-1}mol^{-1}	cal deg^{-1}mol^{-1}	cal deg^{-1}mol^{-1}
$HF(g)$	41.51 ± 0.01[a]	0	0
$LiF(c)$	8.52 ± 0.04	0	0
$LiHF_2(c)$	16.97 ± 0.04	0	1.38 (R ln 2)
		ΔS	ΔS
	ΔS, kcal mol^{-1}	+33.06	31.68
	$T\Delta S$, kcal mol^{-1}	9.857	9.445
	$\Delta H^\circ_{298.16}$, kcal mol^{-1}	13.410	12.998

Uncertainties given are estimated as twice the standard deviation of the mean.

If the proton were assymetric we would expect Rln 2 ± 1.38 for S_0 of $LiHF_2$ and this would lead to a slightly lower enthalpy of vaporization and a slightly less negative heat of formation of HF(by 0.4 kcal mol^{-1}). See Table VIII.

The possibility of this is reduced further by the fact that a Clausius-Clapeyron calculation of the heat of vaporization of HF from $LiHF_2$ by Westrum and Burney [26] give 13.7 kcal mol^{-1}, which is even larger than the vaporization energy given by Cox and Harrop. The work on the (FHF^-) bond was recently summarized in an informal report by the author [27].

V. Heat of Formation of Aqueous HF-Recent Studies

More recently evidence has begun to accumulate concerning the heat of formation of aqueous HF, drawn from completely independent sources.

In Figure 5 we show as the lower line the heat of formation of HF(aq) as a function of H_2O/HF ratio, as listed in TN 270-3 [13]. In the upper curve are shown the results of Cox and Harrop [15]. In between are points representing the heats of formation as found from more recent data. Typically these points are derived from the heat of formation of a fluoride by direct combination of the elements or some other process; combined with a hydrolysis reaction in which HF(aq) is formed. The points are located at the concentration of HF(aq) that was actually formed experimentally. We find definite evidence of a "concensus" that the heat of formation of HF(aq) must lie between the two extremes represented by the upper and lower curves.

These data come from several laboratories. The two BF_3 points (points 1 and 2) represent direct combinations of boron and fluorine as measured at NBS [28] and at Argonne [29], combined with a cycle for the hydrolysis of BF_3 proposed by Hubbard [29]. The three CF_4 points (points 3, 4, and 5) represent the recent determination of the heat of formation NPL [31] and Wisconsin [18]. This could be augmented by a very similar pair of points based on work on CF_4 at Argonne [32]. The NF_3 point was performed completely at Dow Thermal Laboratory [33]. The HF point (point 7) was by directly forming the solution from the elements and water (by King) in our laboratories [34]. The latter point if combined with the heat of solution of HF from TN 270-3 [13] leads to $\Delta H_f(HF(g)] = -65.15$ kcal mol^{-1}. Similar values would also be found from other data points in Figure 4.

One final piece of work may be mentioned in closing. Rodenberg and Vanderzee [35] have recently completed a measurement of the heat of solution of HF in NaOH solution leading to the heat of formation of fluoride ion or of HF at ∞ dilution. By their calculation they find ΔHF at ∞ H_2O is in agreement with the value in TN 270-3. Because the extrapolation to ∞ dilution is several kilocalories per mole this is not necessarily inconsistent with the finding shown in the chart. If confirmed, however, it could mean that the dilution energy (to ∞ dilution) is in error.

The recent review by D. R. Stull and collaborators [36] summarizes in a systematic way much of the material presented above, possibly including some additional material. The validity of such a summary, and the enthalpy of formation derived from it depend strongly upon the weights assigned to the various contributing reactions.

VI. New Work on the Dissociation of F_2 and HF

An important very recent contribution to this subject is made by Dibeler, and co-workers [37] who have measured the dissociation energy of fluorine and of HF. Note that if their two values are taken together, the enthalpy of formation of HF(g) can be calculated, in the same way as in Table VI, and give a value in good agreement with values cited above. However, if their F_2 dissociation energy is combined with the dissociation energy of HF reported by Johns and Barrow [20] a discrepancy of about 3 kcal mol^{-1} is found. This is rather substantially outside the limits suggested by the large aggregation of data on HF(g) given above. A very real problem arises as a result of the new work. If the calorimetric thermochemistry be taken as conclusive evidence of an enthalpy of formation of HF(g) of -64.8 ± 0.5 kcal mol^{-1}, and the work of Dibeler and co-workers be accepted, then an error must be present in the analysis of Johns and Barrow, which is unexpected in view of the very fine consistency of the results they obtained, or as suggested by Dibeler, et al., they have measured vibrational levels above the thermodynamic dissociation level of HF. A further result of the work of Dibeler, et al., is that bond energies calculated on the basis of the dissociation energy of F_2 will be appreciably lower than previously calculated.

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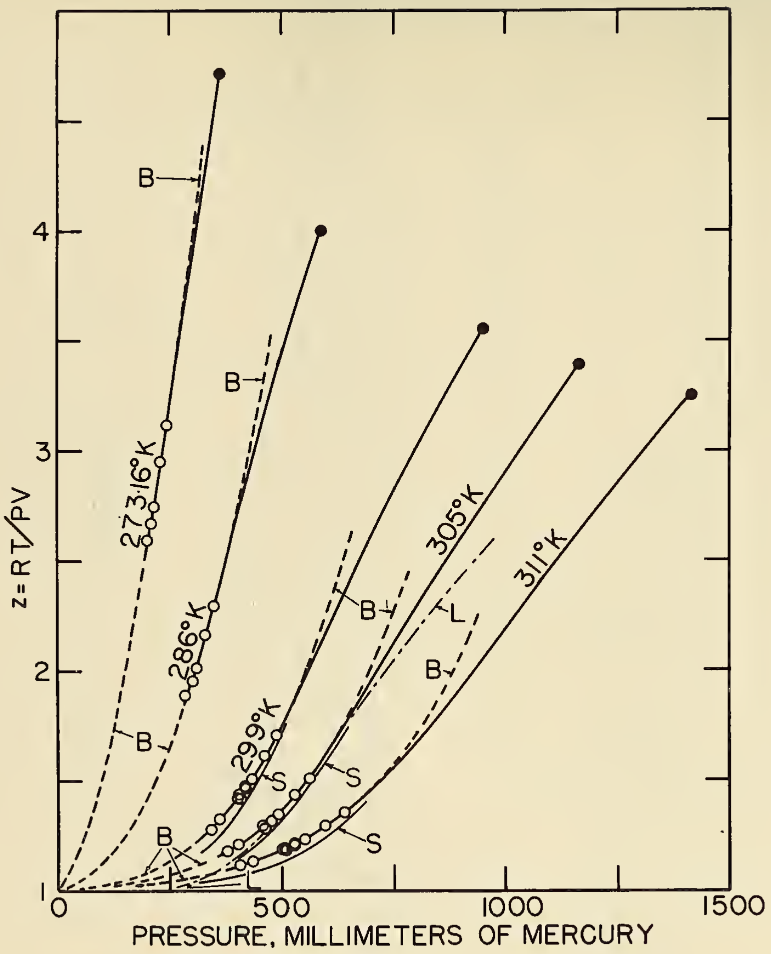

Figure 1

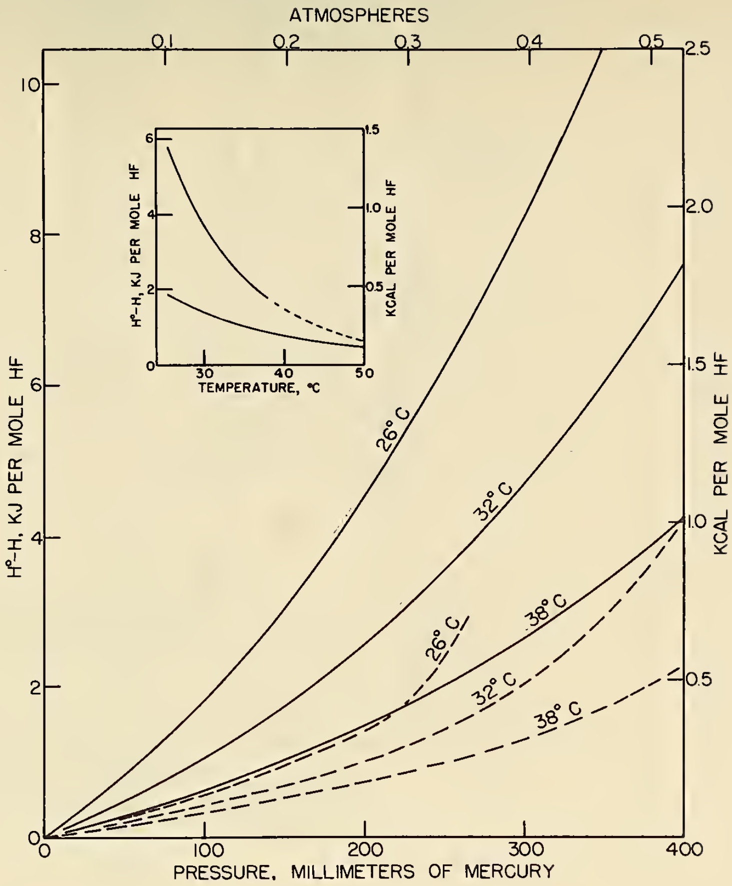

Figure 2

TABLE 1. FLUORINE

Substance	D_0 or $\Delta H°$ (kcal/mole)	Remarks
F(g)		N.B.S. Circ. 500 [9] gives 18.3 for $\Delta Hf°_{298}$. See $F_2(g)$ for extensive later information.
$F_2(g)$	Experimental measurements leading to D_0 or $\Delta H°$ for dissociation have been reported as follows: 66[54], 50 ±6[55], < 45[56], 37.7 at 759 to 1115°K or 38.9 at 1000°K[57], > 45[58], 40-45[59], 37.7[60], 39.9 ±0.8[61], 37.0 ±2[62], 31.5 ±0.9[63], 37.6 ±1.6[64], 37.6 ±0.8[65], 31[66,67], 38 ±0.4[68, 69], 32 ±3[70], 37.5[71], 41.3 ±0.5[73], 37.1[92], 31.6 ±4.3[606], ≤ 39.0[606].	Discussions and calculations of the dissociation energy have been reported by [9, 11, 14, 18, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 89, 90, 91, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 508]. [105] meas. v.p. and ΔH vap. [540] meas. ionization and dissociation by electron impact. [580] est. D_0 values from -34 to +180.
$F_2(\ell)$		[105] meas. ΔH fus.
$F_2(c)$		[105] meas. ΔH trans. (c,I) → (c,II).

Data in tables 1 - 8 are citations from the literature and have not been critically reviewed for this paper.
All numerical values are in kcal $mole^{-1}$ unless otherwise specified.
See [9] for additional references prior to 1949.
Superscript a on ΔHf values for Br and I compounds indicates that such values are based on $Br_2(g)$ or $I_2(g)$ as standard states.

Figure 3. Reproduction of a table listing work published on the dissociation energy of fluorine in the interval about 1950 to 1960. The table is taken from reference [1] and the reference numbers listed refer to the bibliography of reference [1].

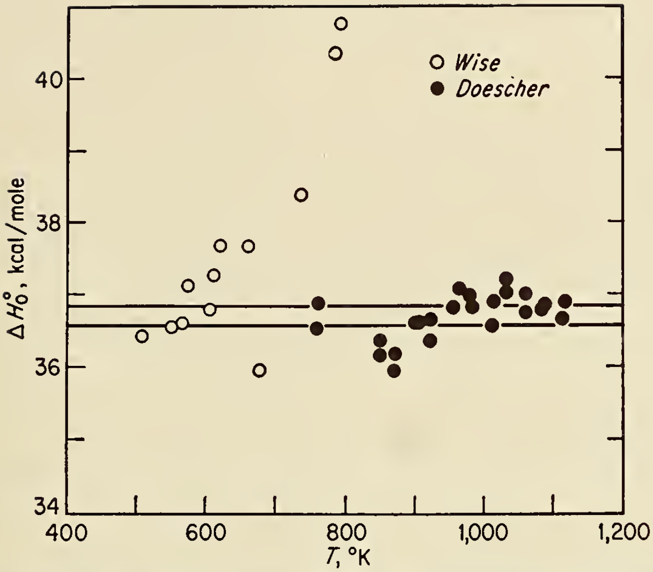

Figure 4 Values of ΔH_0° of dissociation of F_2 from combination of individual equilibrium measurements with $(F_0^\circ - H_0^\circ)/T$ data. [*J. G. Stamper and R. F. Barrow, Trans. Faraday Soc.*, **54**, 1592 (1958), *fig.* 1.]

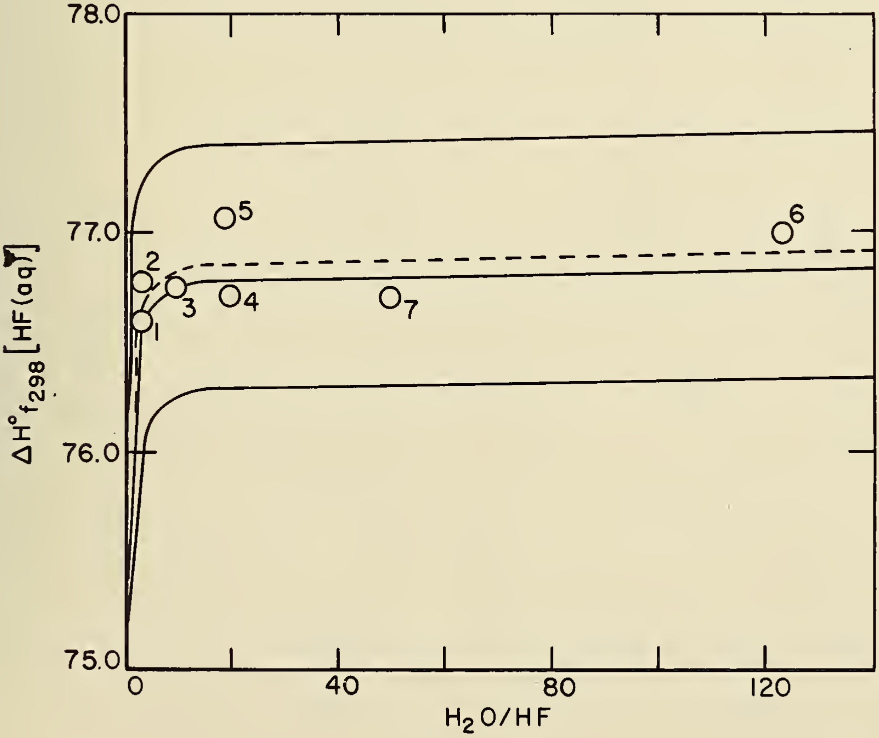

Figure 5

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