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THERMOCHEMISTRY OF INORGANIC FLUORINE COMPOUNDS

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I. Introduction

Thermochemical data on inorganic fluorides are applied practically to energy balancing and equilibria in the fluorochemical and allied industries. In addition, they can be used to rationalize some of the peculiarities of fluorine chemistry. Thus, the almost monopolistic position of cryolite melts in the manufacture of aluminum—and possible ex-

tensions to electrowinning of other metals—has encouraged studies in molten fluoride systems. The use of uranium fluorides for isotope enrichment, fuel recovery, and metal production in the nuclear power industry has prompted thermochemical investigations of these fluorides and of the interhalogen fluorides. Developments in high-temperature thermochemistry of fluorine compounds have followed from the use of fluorides in rocket propulsion, and from attempts to improve tungsten lamp efficiencies by fluoride additions to the lamp gas. At the other extreme, problems arising from fluorides in the environment, such as the lifetime of chlorofluorocarbons in the atmosphere and of fluorides in water supplies, have encouraged studies into stabilities of simple and complex fluorides, often at high dilutions. The jolt to established dogma provided by the discovery of noble gas chemistry and its relation to interhalogen chemistry provides a good example of the usefulness of fluorine thermochemistry in its rationalizing aspect.

Fluorine thermochemistry itself has not been previously reviewed, but has tended to be included in more general reviews and reports, or in data compilations (*141, 123, 151*). The most comprehensive literature survey, covering the years 1949–1961 (*9*), supplements the *N.B.S Circular* and *Notes (203)*. (*N.B.S. Technical Notes* 270–3 to 270–7 issued from 1969–1973 were unfortunately published without literature references.) Subsequent work was conveniently traced from annual issues of the *Bulletin of Chemical Thermodynamics,* and from 1977 to 1979 (May) by accessing the *Chemical Abstracts* data files. Experimental aspects of fluorine thermochemistry are included in two rather dated volumes (*214*), and only general detail will be given in this review.

II. Technique and Key Values

Thermochemical measurements rely directly—or indirectly via chemical standards—on electrical measurements, and these have been simplified in recent years by the introduction of integrated circuitry. Thus the expensive platinum-resistance thermometry associated with bomb calorimetry is being replaced by quartz thermometry, which depends on the linearized temperature variation of frequency of specially cut quartz crystals. [A clear discussion of practical temperature scales is given by Ambrose (*7*).] Voltage and current measurements can be carried out at short intervals using digital voltmeters of appropriate accuracy in place of manually operated potentiometers. Digital timers have largely displaced mechanical clocks. Use of this newer instrumentation does not necessarily mean that all re-

TABLE I

Key Values for $-\Delta H_f^\circ$ [kJ mol⁻¹ (kcal mol⁻¹)] with Corrections (Δ) to Align with CODATA Values

Species	N.B.S. Circ. 500 (1952)[a]	N.B.S. Tech. Note 270/3 (1969)[a]	JANAF Tables (1971)[b]	CATCH Tables (1972)[c]	CODATA Bulletins (1977, 1978)[d]
$F_{(g)}$	−74.5 (−17.8)	−78.99 (−18.88)	−78.91 (−18.86)	−78.99 (−18.88)	−79.39 (−18.97) ± 0.30
Δ	−4.9 (−1.2)	−0.40 (−0.09)	−0.46 (−0.11)	−0.40 (−0.09)	
$F^-_{(g)}$	332.63 (79.5)	270.70 (64.7)	260.2 (62.2)	270.70 (64.7)	250.7 (59.9) ± 0.4[e]
Δ	−77.5 (−18.5)	−15.6 (−3.7)	−5.1 (−1.2)	−15.6 (−3.7)	
$F^-_{(aq)}$	329.11 (78.66)	332.63 (79.5)	—	335.68 (80.23)	335.35 (80.15) ± 0.65
Δ	6.24 (1.49)	2.72 (0.65)	—	−0.33 (−0.07)	
$HF_{(g)}$	268.61 (64.2)	271.12 (64.8)	272.55 (65.14)	273.30 (66.32)	273.30 (65.32) ± 0.70
Δ	4.69 (1.12)	2.18 (0.52)	0.75 (0.18)	0 (0)	
$HF_{(l)}$	—	299.78 (71.65)	—	303.55 (72.55)	

[a] From N.B.S. Circular 500 (203). [b] From JANAF Thermochemical Tables and Supplements (123). [c] From Pedley (177). [d] From Cox (60). [e] This is not a CODATA value but has been calculated using the latest electron affinity value (162) of 3.399 eV at 0 K corrected to 327.96 kJ mol⁻¹ at 298 K.

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cent calorimetry is more accurate than the older determinations, because the limiting factors, especially in fluorine thermochemistry, are often the purity of materials, the stoichiometry of assumed reactions, possible accompanying corrosion reactions, and the correct choice of auxiliary heat values. Thus, adequate analysis of reactants and products is equally as important as good heat measurement. Fluoride analysis has been greatly aided by the introduction of the lanthanum fluoride specific-ion electrode which can be used as an end-point indicator accurate to 0.1% on milligram quantities of fluoride. This electrode has also facilitated the study of metal ion–fluoride equilibria in solution.

In fluorine thermochemistry, two key heat values frequently occur. They are the dissociation energy of difluorine, required for evaluation of fluorine bond energies; and the heat of formation of hydrogen fluoride, a product in hydrolysis, hydrogenation, fluorine combustion, or neutralization reactions. These values have been difficult to measure and have changed considerably over the years. A recommended set of values has been reported in recent CODATA bulletins (60) which are collected in Table I together with older values and corrections to update them.

Some revisions to published values have been made but unfortunately not all authors clearly indicate the key values used.

A. The Dissociation Energy of Difluorine

A recent review (29) on this subject has appeared which, together with an older one (154), covers the literature back to 1922. The most obvious method for estimating the dissociation energy, from the convergence limit of absorption spectra, was difficult for difluorine because the spectrum did not show the usual banded structure. The convergence limit had to be found by examining the pattern of the continuum and comparing it with that of the other dihalogens. The expectation of a monotonic increase from diiodine to difluorine seems to have influenced the interpretation. Values in the range 270–290 kJ mol^{-1} were obtained for $D_0^o(F_2)$. However, by using various Born–Haber cycles, with gaseous or solid fluorides, it soon became obvious that these values were too high. A typical type of cycle was to compare $D_0(MF)$ with $D_0(MCl)$, where M was an alkali metal. Thus for KF and KCl

$$\frac{1}{2}[D_0(F_2) - D_0(Cl_2)] = D_0(K - F) - D_0(K - Cl) + S(KF) - S(KCl)$$
$$+ \Delta H_f(KF) - \Delta H_f(KCl)$$

An average $D_0(F_2) = 157.3 \pm 6.7$ kJ mol^{-1} was obtained from nine such

cycles. This lower value was confirmed by direct pressure measurements on the dissociation. Doescher (71) used a prefluorinated nickel tube heated from 759 to 1115 K in which F_2 and H_2 gases separated by a diaphragm were allowed to exert a differential pressure across a fluorocarbon oil manometer. Wise (237) used gas effusion through a nickel orifice at 500–800 K and at a total pressure of about 10^{-4} mm. Both sets of data were reanalyzed by Stamper and Barrow (217) using a third law treatment to obtain $D_0(F_2) = 157.8 \pm 0.5$ kJ mol^{-1}.

Photoionization of difluorine and chlorine monofluoride appeared to give an even lower value (68), but a reexamination showed that one of the dissociation processes had been ignored (29). In this method fluorine is exposed to monochromatic UV radiation, and the positive and negative ions are observed in a mass spectrometer.

$$F_2 + h\nu \begin{cases} \nearrow & F_2^+ + e \qquad \text{(i)} \\ \rightarrow & F^+ + F^- \qquad \text{(ii)} \\ \searrow & F^+ + F + e \qquad \text{(iii)} \end{cases}$$
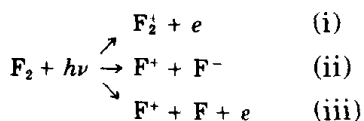
The threshold wavelength for the appearance of F^+ in (iii) has an energy equal to the ionization energy plus the enthalpy of fluorine. However, because some F^+ is generated in (ii) via an excited F_2 state, one needs to subtract this quantity of F^+ (measured by observing the F^- ion) in order to obtain the true threshold at 652.5 Å [equivalent to $D_0(F_2)$ of 157.6 ± 1.0 kJ].

Finally, it has now proved possible, using high-resolution apparatus, to examine the emission-band system (around 1100 Å) generated by microwave discharge in difluorine (54). Vibrational levels of the ground state up to $v = 22$ show that the convergence limit is above 12,830 cm^{-1}. However, no regular pattern is followed and there is no unambiguous extrapolation to infinity. An estimate of $12,920 \pm 50$ cm^{-1} leads to $D_0(F_2) = 158.8 \pm 0.6$ kJ mol^{-1}, the CODATA value.

B. The Heat of Formation of Hydrogen Fluoride

The standard enthalpy of formation of monomeric HF is a hypothetical state that must be related to that of the real associated liquid, gas, or aqueous solution met in calorimetry. Considerable difficulty has been encountered in allowing for the heat of association, which varies with temperature and pressure. For example, the presence of traces of water can affect the polymerization by entering into the hydrogen bonding (30); the treatment of results will depend on the association model adopted. The magnitude of corrections for gas imperfections has

been minimized by carrying out combustions in fluorine to form HF at 100°C (234) or to form liquid HF (132), and heats of solution have been measured from HF at 0.2 atm (225). There are two sets of conflicting PVT data. The earlier set by Long, Hildebrand, and Morrell (158) was treated assuming a monomer–cyclic hexamer mixture, and the latter, by Strohmeier and Briegleb (221), assumed a full set of linear polymers up to $(HF)_9$. The former set has been recalculated (8), assuming the linear polymer model, to give a better overall data fit, but large discrepancies with Briegleb's results remain at lower pressures. The latter results have been confirmed by Franck and Meyer's heat capacity measurement (92) determined by measuring the temperature gradient along a nickel capillary subjected to an applied potential when HF or N_2 flowed through. The constant specific heat of HF above 105°C was assumed to be that of the monomeric gas; hence H_T(ideal) $-$ H_T(real) can be calculated at each temperature and pressure.

The nonideality correction has been avoided by using $HF_{(l)}$ as the standard state (132), determined by fluorine bomb calorimetry, and then measuring its heat of solution and neutralization. The value $\Delta H_f^\circ(F_{(aq)}^-)$ was derived by allowing for the heat of ionization of water and heats of dissociation of HF and HF_2^- present in HF solutions. These results are about 0.8 kJ more negative than those derived from the heat of solution in NaOH of the gas at about 0.2 atm allowing for gas nonideality. King and Armstrong's measurement on the enthalpy of the $H_{2(g)} + F_{2(g)}$ reaction with the addition of water to obtain $\Delta H_f^\circ(HF \cdot 50H_2O_{(l)})$ extrapolate to a more positive value of $\Delta H_f^\circ(F_{(aq)}^-)$, possibly because of errors in the corrosion heat allowance (145).

Another stratagem to avoid nonideality of the gas state is to compare heats of formation of fluorides derived from fluorine combustion on the element, with heats of hydrolysis determined directly or indirectly, as in

$$M + \frac{n}{2} F_2 \; = MF_n \qquad\qquad \Delta H_1$$

$$MF_n + nH_2O = M(OH)_n + nHF_{(aq)} \qquad \Delta H_2$$
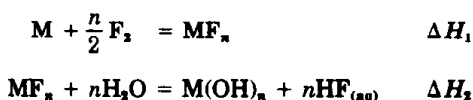
where $M(OH)_n$ represents a lower polybasic acid, or a complex fluoroacid, rather than the hydroxide. Ideally, one would like to compare fluorine and oxygen bomb calorimetry, since the heat of formation of the hydroxo species should be linked to that of the oxide (see p. 34). It follows that

$$\Delta H_f(HF) = \frac{1}{n}(\Delta H_1 - \Delta H_2) + \Delta H_f(H_2O) - \frac{1}{n}\Delta H_f(M(OH)_n)$$

TABLE II

INDIRECT DERIVATION OF ΔH_f^o ($F_{(aq)}^-$) IN kJ mol^{-1}

Heats of reaction measured	Heats of formation required	Derived $-\Delta H_f^o(F_{(aq)}^-)$
1 Mg(OH)$_2$ + HF$_{(aq)}$; MgO + H$_2$O (132)	MgF$_2$ (196), MgO	335.8 ± 0.9
2 BF$_3$ + HF$_{(aq)}$; B + O$_3$ + HF$_{(aq)}$ (134)	BF$_3$ (73)	335.6 ± 0.4
3 BF$_3$ + HF$_{(aq)}$; H$_3$BO$_3$ + HF$_{(aq)}$; B$_2$O$_3$ + F$_2$ (133)	BF$_3$	335.3 ± 0.4
4 NF$_3$ + H$_2$ + H$_2$O (212)	NF$_3$ (159)	335.7 ± 0.4
5 (C$_2$F$_4$)$_n$ + F$_2$; (C$_2$F$_4$)$_n$ + O$_2$ + H$_2$O (100)		336.2 ± 0.4
6 SiO$_2$ + F$_2$; SiF$_4$ + HF$_{(aq)}$; SiO$_2$ + HF$_{(aq)}$ (230)	SiF$_4$ (238), SiO$_2$	336.2 ± 0.4
7 IF$_5$ + H$_2$O (240)	IF$_5$ (206), IO$_3^-$	335.8 ± 0.4
8 MoF$_6$ + OH$^-$; MoO$_3$ + OH$^-$ (165)	MoF$_6$ (204), MoO$_3$	334.1 ± 0.5

Thus, errors in all the heats, apart from the precisely known water value, are decreased n-fold in the required heat. The hydrolysis heat ΔH_2 is always much less than ΔH_1 and can be measured less precisely. The reactions involved in reactions 2, 3, and 6 of Table II have been used in the CODATA evaluation of $\Delta H_f(F_{(aq)}^-)$, although in theory reactions 7 and 8 should lead to more accurate values. In practice this may not be true. Thus the fluorination of iodine produces some IF$_7$, together with the bulk of IF$_5$, and errors in estimating the mixture can cause uncertainty in the final value of ΔH_f(IF$_5$). The hydrolysis heat for the reaction

$$IF_{5(l)} + (n+3)H_2O = (HIO_3 + 5HF) \cdot nH_2O$$
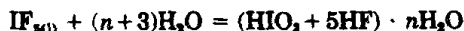
involves the heat of formation of HIO$_3$, which is not determined by oxygen bomb calorimetry but indirectly by reactions such as (IO$_3^-$ + 5I$^-$) → 3I$_2$.

The fluorination of Mo was straightforward, with less than 0.1% MoF$_5$ being admixed with MoF$_6$, but the alkaline hydrolysis was particularly slow (1–3 hours), presumably because of polyoxyanion equilibration in solution, which accounts for the divergence between published values (161, 165).

An ideal derivation would be via direct fluorination of Re and hydrolysis of ReF$_7$ to perrhenic acid, especially since ΔH_f^o(Re$_2$O$_7$) has been determined by oxygen combustion of Re. However, ReF$_6$ is the main fluorination product under normal conditions. It seems that further work on iodine fluorination to produce enhanced yields of the heptafluoride, and the hydrolysis of IF$_7$ to periodic acid, is potentially the best route for improving the $\Delta H_f^o(F_{(aq)}^-)$ value.

A determination of the heats of solution of germanium dioxide and tetrafluoride in aqueous hydrogen fluoride, to give the same final composition of fluorogermanic acid, when taken in conjunction with the precisely known heats of formation of the solids should also yield a precise value of $\Delta H_f(HF_{(aq)})$ from the overall reaction heat of

$$GeF_{4(s)} + 2H_2O_{(l)} = GeO_{2(s)} + 4HF_{(aq)}$$
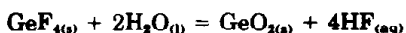
These key values have been satisfactorily linked by measuring the onset of photoionization or the convergence of spectral band systems in the dissociation of HF (69), whence

$$\Delta H_f(HF_{(g)}) - \Delta H_f(F_{(g)}) = \Delta H_f(H_{(g)}) - D(HF)$$

III. Survey of Methods for Heats of Formation of Fluorides

A. FLUORINE BOMB CALORIMETRY AT CONSTANT VOLUME

This technique, introduced by von Wartenberg (234), has been developed into a precision technique giving results reproducible to 0.05% or better at the Argonne National Laboratory by Hubbard and co-workers since 1960 (214). It is essentially similar to oxygen bomb calorimetry modified to withstand the reactivity of fluorine. The main materials of construction are nickel, monel metal (Ni, Cu, Fe), or stainless steel (Fe, Ni, Cr), together with aluminum, lead, copper, and polytetrafluoroethylene (PTFE) as gasket and packing materials. Since none of these materials is totally inert to fluorine, the combustion bomb is carefully prefluorinated to form a coherent layer of a protective fluoride whose parabolic growth rate is negligible during an experimental run. The protective film has to be maintained in an anhydrous condition. Exposure of the PTFE packing and sleeving is also minimized to avoid its combustion. The fluorine is fractionated by low-temperature distillation to obtain a purity of at least 99.5%. Impurities can be kept below 0.1% and are estimated by the residual volume which remains after shaking with mercury. Each sample combusted presents its own problems, and appropriate modifications in the support and method of ignition are required. Materials which ignite spontaneously in fluorine, such as sulfur, can be used as kindlers to help combustion of more resistant materials. Samples can be in wire, block, or pellet form, or enclosed in metal foils. It is not unusual for metal samples to melt and leave unreacted beads. Metal fluoride powders or discs can be used to support the specimen and prevent damage to the calorimeter walls. Residual metal is determined from the hydrogen released on acid dissolu-

tion. An extreme example of partial fluorination was encountered in determining $\Delta H_f(NiF_2)$ when only half the metal was converted to fluoride. Heats evolved from metal impurities can be estimated assuming their presence in particular forms and combustion to appropriate fluorides. Alternative choices can sometimes be made—e.g., with carbides or borides as impurities—and errors are minimized by using the purest materials available.

French workers have developed a series of double-compartment bombs of small volume in which the sample volume is initially separated from the larger gas volume (48). This allows combustions to be carried out on 50-mg samples but at lower precisions than with the larger bombs.

Only six other centers have operated similar metal bomb calorimeters, mainly modeled on the Hubbard design, and it is therefore of interest to note that Gross and co-workers have been intrepid enough to use a simple two-compartment glass apparatus separated by a break-seal for fluorine combustion (5 atm F_2). Their results were in excellent agreement with those obtained in metal bombs (107).

Although most of the fluorine calorimetry has been done with the elements, it has been used to burn oxides, carbides, nitrides, and chalcogenides and hence determine their heats of formation. In some instances it has proved superior to oxygen bomb calorimetry. Thus the oxidation of boron tends to be incomplete because of oxide coating, whereas fluorination produces gaseous boron trifluoride without surface inhibition. A summary of modern fluorine calorimetry results is assembled in Table III.

TABLE III

ENTHALPIES DETERMINED BY FLUORINE BOMB CALORIMETRY

Group II	BeF_2 (53, 175); MgF_2 (196); ZnF_2 (196); CdF_2 (193)
Group III	BF_3 (73, 133); BN (239); BP (108); B_2O_3 (134); AlF_3 (195); GaF_3 (142); YF_3 (194); YbF_3 (142); SmF_3 (141); HoF (143); ErF_3 (144); ThF_4 (226)
Group IV	CF_4 (72, 100); SiF_4 (238); SiC (101a); SiTe, $SiTe_2$ (36, 37); GeF_4 (1, 104); GeF_2 (5); GeO_2 (104); GeS (4); SnF_4 (2); TiF_4 (102); ZrF_4 (103); HfF_4 (102); HfB_2, ZrB_2 (136)
Group V	PF_3 (137, 197); PF_5 (170); AsF_5 (167); SbF_5 (37); VF_5 (135); NbF_5, TaF_5 (101)
Group VI	SF_6, SeF_6, TeF_6 (169); NSF, NSF_3 (171); Li_2Se (6); MoF_6 (204); MoS_2 (166a); WF_5, WF_6 (168, 201); WB, W_2B, W_2B_5 (155); UF_4, UF_6 (130, 205)
Group VII	IF_5 (206); BrF_3 (218)
Group VIII	NiF_2 (196a); RuF_5 (179)

B. Fluorine Flame Calorimetry at Constant Pressure

Fluorine flame calorimetry is a logical extension of oxygen flame calorimetry in which a gas is burned in excess of gaseous oxidant (214). The precision does not reach that of the oxygen flame calorimeter in which, for example, $\Delta H_f(H_2O)$ was determined with a standard deviation of 0.01%. Combustions of H_2, NH_3 (8), and fluorinated hydrocarbons are typical applications, but the uncertain nonideality corrections of $HF_{(g)}$ prevent full realization of the inherent accuracy.

C. Explosion (Decomposition) Calorimetry

Nitrogen trifluoride is a kinetically inert gas, but when sparked or heated can fluorinate substrates and release nitrogen. Sulfur, for example, is quantitatively converted to SF_6 using NF_3 at 5 atm (231). Similarly, boron is converted to BF_3 (159) and CF_3CN to CF_4 (232). Nitrogen trifluoride has some advantages over difluorine. It is safer to handle, and double-compartment bombs to avoid self-ignition are not required. However, some self-dissociation has to be measured and corrections made.
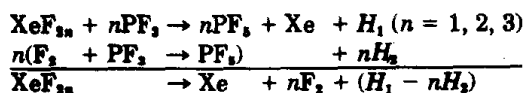
$$S + 2NF_3 \rightarrow SF_6 + N_2$$
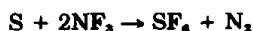
Explosive hydrogenation has been employed with gaseous fluorides and the liberated HF dissolved *in situ* in water. This requires a platinum-lined bomb to minimize corrosion.

Thus from the heat of reaction of

$$\tfrac{3}{2}H_2 + NF_3 \rightarrow 3HF_{(aq)} + \tfrac{1}{2}N_2$$
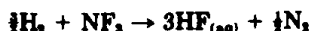
one can obtain either the enthalpy of NF_3 or of aqueous HF (212). Hydrogenation has also been applied to chlorine oxyfluorides (48).

Phosphorus trifluoride has been used as a reactant gas in calorimetry to act as a fluorine acceptor rather than donor. The heats of formation of xenon fluorides have been calculated from the reaction heats (137):

$$\begin{array}{ll}
XeF_{2n} + nPF_3 \rightarrow nPF_5 + Xe & + H_1 \ (n = 1, 2, 3) \\
\underline{n(F_2 + PF_3 \rightarrow PF_5)} & \underline{+ nH_2} \\
XeF_{2n} \qquad \rightarrow Xe & + nF_2 + (H_1 - nH_2)
\end{array}$$

The xenon fluorides, especially the difluoride, could also be used as calorimetric gases with possible applications for organic fluorides or metal carbonyls [e.g., $Mo(CO)_6 \rightarrow Mo(CO)_nF_{6-n} \rightarrow MoF_6$].

The heats of formation of the fluoroamines $CF_n(NF_2)_{4-n}$ (213), $CF_2(OF)_2$ (91), KrF_2 (109), and F_2O_2 (146) have been determined by thermal decomposition.

D. Solid-State Calorimetry

The heat of reduction of a fluoride with metal has been measured for (*106*)

$$\tfrac{1}{2}PbF_2 + Al \rightarrow AlF_3 + \tfrac{3}{2}Pb$$

The components need to be oxide-free and finely divided. The enthalpy of formation found for AlF_3 was in reasonable agreement with the fluorine bomb value. The method is of limited scope.

E. Solution Calorimetry

Solution calorimetry has been the most widely applied type of calorimetry because it needs relatively simple apparatus, and a wide choice of liquid reagents is available. Much of silicate thermochemistry, for example, has been based on the hydrofluoric acid solution calorimeters using platinum or silver vessels and fluorinated gaskets (*90, 214*).

1. Fluorosulfuric Acid

Fluorosulfuric acid has been recently introduced as a calorimetric medium. It has the advantage that ordinary glass calorimeter vessels can be used, and that the liquid is easily purified and recovered by distillation. [A slight excess of SO_3 over the $HFSO_3$ composition is present in distillates from glass which does not affect calorimetric measurements in most applications (*186*). It is easily adjusted by addition of HF.] Heats of formation of fluorosulfates, obtained by displacement or solvolytic reactions, can be measured as well as those of simple and complex fluorides by neutralization or displacement reactions. Heats of solution in fluorosulfuric acid, a strong acid, can be related to ionization of solutes in this solvent (*187*). This is especially useful as a criterion of base strength (proton acceptance). The heat of transfer of base from HSO_3F to CCl_4 (i.e., the difference in solution heats between the two solvents) for a series of 35 amines was linearly related to the pK_a values measured in aqueous solutions. A similar relation held for 52 carbonyl bases (*11*). (Carbon tetrachloride is used as a reference phase to assess the heats of solution of the un-ionized solutes.) For even weaker bases, such as aromatic hydrocarbons, their protonation can be enhanced by increasing the acidity of HSO_3F with SbF_5. Heats of protonation were measured in such media at $-60°C$ using CCl_4 at 25°C as the reference medium (*11a*), and again the base strengths correlated linearly with pK_a values obtained this time in anhydrous HF at 0°C. In later work, the acidity of SbF_5 itself has been used to generate alkyl

carbonium ions in solvents such as SO_2F_2, SO_2ClF, CH_2Cl_2, and SO_2, and heats of ionization measured mainly at $-55°C$ (10). Heats of ionization of alkyl chlorides obtained in $SO_2ClF-SbF_5$ media correlate with gas-phase values obtained by ion cyclotron resonance techniques. It should be possible to obtain the enthalpies of a whole range of carbonium-complex fluorides from these data if some additional auxiliary heats are measured. Gutmann's donor number concept (110) (the heat of interaction of bases with $SbCl_5$ in CH_2Cl_2) is obviously extended by these measurements on large classes of related compounds.

2. Bromine Trifluoride

Bromine trifluoride was advocated as a liquid reaction medium for calorimetry with certain advantages over fluorine bomb calorimetry (188). Reactions would be homogeneous and fast; thermally unstable fluorides such as gold(III) fluoride could be handled; the solvent itself was easily purified by distillation or fractional freezing, and was self-dehydrating, unlike anhydrous hydrogen fluoride; and only simple calorimetric apparatus was required. In addition, the enthalpies of a wide range of complex fluoro salts were accessible from heats of neutralization of the acid–base system in bromine trifluoride. These salts cannot be made heterogeneously in the fluorine bomb, under the usual conditions. A nickel-plated brass calorimeter of the type described by Gerding, Leden, and Sumner (214) with minor safety modifications was used for most reactions.

For the more vigorous reactions, a twin-cell calorimeter was devised (188). It consisted of two nickel cylinders connected by a stainless steel needle valve and tubing and held rigidly to a metal top-plate. The cylinders and connections were immersed in a wide-necked Dewar vessel containing carbon tetrachloride which would react mildly with any BrF_3 that escaped. Bromine trifluoride contained in one cylinder was transferred to the solid contained in the other cylinder by opening the valve and applying controlled suction. All measurements were made externally on probes in the carbon tetrachloride.

However, a complication arose because in the liquid phase bromine, released on fluorination, only equilibrated slowly with the bromine trifluoride. The vapor-phase equilibration $Br_2 + BrF_3 \rightleftharpoons 3BrF$ surprisingly occurs within minutes at $25°C$ (219). Hence BrF_3 was first equilibrated with an excess of Br_2. Then the heat of addition of further Br_2 was small and reached equilibrium within 5 min provided the BrF_3/Br_2 mole ratio was held within limits of 7 to 6.5. These mixtures have additional advantages in that the BrF_5 content, which is reported

to form via $2BrF_3 \rightleftharpoons BrF + BrF_5$ is suppressed and the vigor of reactions is moderated.

The actual composition present in the Br_2/BrF_3 mixture is not known, and any fluorination reaction may be a composite reaction of BrF, BrF_3 and BrF_5. It is not necessary to assume that BrF_3 is the reactive constituent, although this is probable. Consider the fluorination of a species X—a metal, oxide, oxysalt, halide, etc.—to the fluoride XF_n by a mixture of bromine fluorides BrF_{Qi}. The general reaction is

$$X + n \sum_i \frac{qX_i}{Q_i} (BrF_{Qi}) = XF_n + \frac{n}{2} \sum_i \frac{qX_i}{Q_i} (Br_2)$$
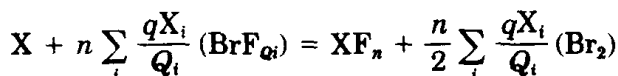
where qX_i is the fraction of X converted to XF_n by a particular bromine fluoride and $\Sigma_i qX_i = 1$.

The corresponding enthalpy change is

$$\Delta H_1 = (H_{XF_n} - H_X) - n \sum_i \frac{qX_i}{Q_i} (H_{BrFQi} - \tfrac{1}{2} H_{Br_2})$$

Similarly, the enthalpy change for converting Y to YF_m would be

$$\Delta H_2 = (H_{YF_m} - H_Y) - m \sum_i \frac{qY_i}{Q_i} (H_{BrFQi} - \tfrac{1}{2} H_{Br_2})$$

If we assume $qX_i = qY_i$ for all values of i (i.e., there is no selectivity of attack by the different bromine fluorides) and that the enthalpies of bromine and its fluorides are not significantly different in the product solutions, then the bromine fluoride values are eliminated by subtraction of the enthalpy changes

$$m\Delta H_1 - n\Delta H_2 = m(H_{XF_n} - H_X) - n(H_{YF_n} - H_Y)$$

and the enthalpy of any one substance can be derived from ΔH_1, ΔH_2, and the known enthalpies of the other three.

The method was checked by showing the consistency of the heat of formation of a $BrF_3 \cdot 7.0Br_2$ equilibrated mixture derived from a variety of reactants (Mo, KIO_3, KBr, K_2SO_4, and $K_2S_2O_8$) (188).

The heat of formation of $BrF_{3(l)}$ obtained from adiabatic calorimetry on Br_2/F_2 gas mixtures implies an exothermic heat of solution of 18.4 kJ for the Br_2 in the BrF_3/Br_2 mixture and is consistent with the non-equilibrated heats of solution measured (218).

The heats of formation of $SnF_{4(s)}$ and $SbF_{5(l)}$ were measured by dissolution of the elements in BrF_3/Br_2 and can be compared with some later values (Table IV).

The fluorine bomb value for SbF_5 is probably low because of the vis-

TABLE IV

COMPARISON OF ENTHALPIES (kJ mol⁻¹) BY DIFFERENT CALORIMETRIES

	BrF$_3$–Br$_2$	F$_2$ bomb	Hydrolysis (M·NaOH)
SnF$_{4(s)}$	1136 ± 4.6 (189)	1171 ± 1.4 (2)	—
SbF$_{5(l)}$	1379 ± 6 (189)	1337 ± 17 (13)	1364 ± 8 (42, 163)

cous coating of pentafluoride, or Sb(III)–Sb(V) mixed fluorides, likely to form on antimony during combustion.

Heats of formation of ternary fluorides of Group IV and V elements were measured from heats of neutralization in pure BrF$_3$. Values below 19 kJ mol⁻¹ indicated acid or base strengths below the maximum and the derived sequence of base strengths K ≃ Ag > Na > Ba with respect to Sb as the acid, or of acid strengths Sb > Ta > Sn with respect to K as base, were in agreement with strengths deduced from electrical-conductance measurements and observations on solvolysis of salts in BrF$_3$ (189).

Bromine trifluoride calorimetry has considerable development potential both with respect to improved accuracy and with respect to the range of materials which can be examined. Thus the more insoluble or refractory materials could be reacted in "acid" or "basic" solutions in BrF$_3$ or even in molten acids or bases at higher temperatures. (The ^{18}O/^{16}O ratio in rocks can be measured on the oxygen released by dissolving minerals in such melts.)

3. Aqueous

Last but not least of the liquid calorimetric media are aqueous solutions used in the hydrolysis of simple and complex fluorides. Stepwise replacement of F by OH occurs, and mixed products are not unusual. Thus the BF$_4^-$ ion hydrolyzes to species BF$_n$(OH)$_{4-n}^-$ and one has to ensure that the same product composition is formed in the auxiliary heat experiments (99). The problem is accentuated when polynuclear species form, as the equilibration can be slow. The inconsistencies in the heats of alkaline hydrolysis of MoF$_6$ and WF$_6$ found by various authors and of the enthalpy of SbF$_5$—derived by assuming SbF$_5$ and Sb$_2$O$_5$ dissolved in 10 M HF produced the same species in solution—illustrate the difficulties. It is as well to confirm enthalpies of higher valent fluorides obtained by hydrolysis by alternative nonaqueous methods, especially since uncertainty in the ΔH_f°(F$_{(aq)}^-$) value is multiplied in the derived enthalpy. The advantage of hydrolysis methods, apart from the simplicity of technique, is that the heats are small and one can tolerate

a relatively large absolute measurement error, as compared with the direct highly exothermic fluorinations.

Certain gaseous fluorides have been regarded as stable to hydrolysis, and it was therefore unexpected when Cady showed that ClO_3F and SO_2F_2 could be rapidly hydrolyzed in dilute alkali solutions (47). This was confirmed calorimetrically when it was shown that the rate of hydrolysis measured calorimetrically was dependent on mass transfer of gas across the gas–water interface. A bell-type calorimeter was used to overcome this problem (49, 51). This type of calorimeter can be used for any gas–liquid reaction and is much more effective than passage of gas through sintered discs into solution.

Heats of precipitation have been employed to determine the enthalpies of sparingly soluble simple and complex fluorides: for example, that of calcium fluoride by adding solid calcium chloride to a solution of excess sodium fluoride saturated with calcium fluoride (88), and of lead chlorofluoride by adding sodium fluoride solution to a saturated lead chloride solution (50).

F. Equilibrium Measurements

Entropies can be calculated or estimated, and hence enthalpies can be derived from equilibrium measurements. Gaseous entropies are calculated by statistical mechanics using experimental or estimated molecular dimensions and fundamental frequencies (93). For solids, numerous methods based on additivity rules, or regularities in series of compounds, are available. Khriplovich and Paukov (140), for example, list 20 such relationships and were able to estimate entropies to about 1%. Empirical equations are also available for ion entropies (59).

The need for entropy values is bypassed when the van't Hoff equation $(d \ln K/dT) = \Delta H/RT^2$ is used. This can be integrated, either assuming ΔH is temperature-independent, or by incorporating a specific heat–temperature variation. This is the so-called second law method which contrasts with the third law method. In the latter method, the standard enthalpy is obtained from each equilibrium constant using free-energy functions of all the species present, for example

$$\Delta H^c_{298} = -RT \ln K - T\Delta \left[\frac{G^c_T - H^c_{298}}{T} \right]$$

An interesting, but controversial, article on the analysis of equilibrium data has appeared (94). The establishment of true equilibrium is tested by concordance between enthalpies derived from second and third law treatments.