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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-

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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 (65.32)	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.

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.

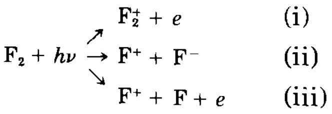
A. THE DISSOCIATION ENERGY OF DIFLUORINE

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 $D_0^{\circ}(F_2)$. 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

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

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.



$$F_2 + h\nu \begin{array}{ll} \nearrow F_2^+ + e & \text{(i)} \\ \rightarrow F^+ + F^- & \text{(ii)} \\ \searrow F^+ + F + e & \text{(iii)} \end{array}$$

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 $H_T\text{(ideal)} - H_T\text{(real)}$ 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

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

$$MF_n + nH_2O = M(OH)_n + nHF_{(aq)} \qquad \Delta H_2$$

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° ($F^-_{(aq)}$) IN kJ mol^{-1}

	Heats of reaction measured	Heats of formation required	Derived $-\Delta H_f^\circ(F^-_{(aq)})$
1	$Mg(OH)_2 + HF_{(aq)}$; $MgO + H_2O$ (*132*)	MgF_2 (*196*), MgO	335.8 ± 0.9
2	$BF_3 + HF_{(aq)}$; $B + O_2 + HF_{(aq)}$ (*134*)	BF_3 (*73*)	335.6 ± 0.4
3	$BF_3 + HF_{(aq)}$; $H_3BO_3 + HF_{(aq)}$; $B_2O_3 + F_2$ (*133*)	BF_3	335.3 ± 0.4
4	$NF_3 + H_2 + H_2O$ (*212*)	NF_3 (*159*)	335.7 ± 0.4
5	$(C_2F_4)_n + F_2$; $(C_2F_4)_n + O_2 + H_2O$ (*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	$IF_5 + H_2O$ (*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 theorv 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 $\Delta H_f(IF_5)$. 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 $(IO_3^- + 5I^-) \rightarrow 3I_2$.

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 $\Delta H_f^\circ(Re_2O_7)$ 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 $\Delta H_f^\circ(F^-_{(aq)})$ 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 $\Delta H_f(\mathrm{HF_{(aq)}})$ from the overall reaction heat of

$$\mathrm{GeF_{4(s)} + 2H_2O_{(l)} = GeO_{2(s)} + 4HF_{(aq)}}$$

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

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

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 dissolution. 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_3 (*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*):

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

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*)

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

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 nonequilibrated 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 $K \simeq Ag > Na > Ba$ 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_2O_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 $\Delta H_f^\circ(F^-_{(aq)})$ 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

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

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.

1. *Solid–Gas Equilibria*

Equilibria between gas and solid phases can be established rapidly at higher temperatures, and equilibrium constants determined from the gas compositions. Complex fluorides such as fluoroborates dissociating to a single gas (*105*) or donor–acceptor adducts giving two gases (*160*) can be studied under static conditions. More use has been made of flow methods in which a gas ratio is measured. Thus, the HCl/HF ratio obtained by passing HCl over a fluoride, or HF over a chloride (*119*); the H_2O/HF ratio from pyrohydrolysis of fluoride (*207*); or the H_2/HF ratio from hydrogen reduction (*124*) have all been exploited. It should be noted that pyrohydrolysis can occur inadvertently in experiments in which moisture has not been rigorously excluded (Section III,F,4).

A scale of fluorinating ability can be drawn up by deriving the free-energy differences between component couples, $(MF_n - MCl_n)/n$, from HCl/HF ratios. Mixed couples can then be used to derive other values. A heat of formation of PF_3 was found from the reaction (*76*)

$$2PCl_3 + 3CaF_2 \rightarrow 2PF_3 + 3CaCl_2$$

The H_2/HF ratio was also used to assess the reduction of UF_4 in a LiF/BeF_2 melt of interest for a possible breeder reactor system (*98*):

$$UF_{4(soln)} + \tfrac{1}{2}H_2 \rightarrow UF_{3(soln)} + HF$$

2. *Vapor Transport*

The transport of solid material via gas-phase intermediates occurs in many industrial processes (*199*). The transport of tungsten via volatile halides has been examined in detail to improve lamp efficiencies. Tungsten fluorides dissociate above 3300 K and deposit tungsten onto hot sites on tungsten filaments. Thermodynamic data on relevent reactions were obtained by measuring the total tungsten transported in an argon gas stream containing a small amount of fluorine introduced in the form of a gaseous fluoride. [The change in conductivity of a hot wire was followed (*70*).] The weight of tungsten "dissolved" in the gas was determined by burning the wire under static conditions to give the molar ratio $n(W)/n(F_2) = R$, which was related to the partial pressures of species by

$$R = \frac{P_W + P_{WF} + \cdots + P_{WF_6}}{0.5P_F + P_{F_2} + 0.5P_{WF} + \cdots + 3P_{WF_6}}$$

At 2000 K, the maximum amount of W dissolved corresponded to

$R = 0.5$, the species WF_4. The maximum transport rate was due to

$$W + 2WF_6 \rightarrow 3WF_4$$

Equilibrium constants involving each compound were evaluated using the partial pressures by the third law method. Accepting the heats of formation of WF_5 and WF_6 obtained from bomb calorimetry, the values for WF_n ($n = 1$ to 4) could be extracted by iterative fitting to partial pressure data. The $W/O_2/F_2$ and $W/S/F_2$ systems were also examined to give heats of formation of tungsten oxo- and thiofluorides. This experimentally simple technique yields thermodynamic data on high-temperature species inaccessible to conventional calorimetry.

An example of transport relevant to aluminum production

$$6NaF + Al \rightarrow Na_3AlF_6 + 3Na$$

was examined by transpiring the sodium vapor in argon (*66*). The enthalpy of cryolite could be determined relative to NaF. Similar transpiration studies on equilibration between element and higher halide yield an enthalpy value for AlF (*148*).

3. *Gas Dissociation*

Difluorine dissociation provides the simplest example of symmetric cleavage at comparatively low temperatures. The facile dissociation

$$N_2F_4 \rightleftharpoons 2NF_2$$

has been followed most accurately by the pressure increase and least so from the UV absorption of the radical (Table V). The latter can be monitored directly from the ESR line spectrum allowing for changes in the Boltzmann distribution, or by ionizing the radical to NF_2^+. The enthalpy of the radical can then be obtained via a second law treatment of the equilibrium. Similar methods have been applied to the dissociation of $S_2O_6F_2$ (*75, 164, 220*), S_2F_{10} (*21*), and the mixed dimer $F_2N{-}NO$ (*128*). The dissociation of CF_3CN

$$2CF_3CN \rightleftharpoons C_2F_6 + C_2N_2$$

presumably proceeds via short-lived radicals, and the neutrals are measured (*232*).

4. *Mass-Spectral Methods*

Vapor-phase analysis by means of a mass spectrometer built into a reaction apparatus has provided identification of transient species generated at high temperatures and low pressures.

A molecular beam generated by reaction in a Knudsen cell—a

TABLE V

HEAT OF DISSOCIATION OF TETRAFLUOROHYDRAZINE

Method	ΔH° (kJ mol^{-1})	Reference
$(dP/dT)_v$	83.3 ± 2.1 85.8 ± 0.8	*127* *80*
ESR	80.8 ± 4.2 82.8 ± 5.4	*178* *74*
UV	86.6 ± 8.2	*55*
Mass spectrometry	90.0 ± 6.7	*112, 56*
Shock wave	87.5 ± 1.7	*82*
Analysis of literature	87.9 ± 3.8	*174*

constant-temperature container with a well-defined orifice an order smaller in size than the mean free path—is ionized by electron bombardment, and the ions are extracted into a compact mass spectrometer. Low resolutions are adequate because relatively few species, including isotopic variants, can form from known starting materials. Background gas generated by radiation from the hot cell can produce interference. Hence it is usual to locate the beam origin using a small sector and to interrupt the beam to produce an ac output easily differentiated from a high dc background.

To investigate high-temperature equilibria, the gaseous species are identified from their parent ions and the relative intensities of ions as a function of temperature help to define the reactions proceeding in the Knudsen cell. The ion current–electron-accelerating voltage curves determine the appearance potential at which the ion is first observed, and intensities are measured at 1–3 eV above this value to prevent ion fragmentation.

The equilibrium constants can be approximated by ratios of ion currents in some instances; otherwise, the currents are converted to partial pressures by comparison with the evaporation of known amounts of a standard material. Various geometric corrections (K) such as the solid angle subtended by the sample at the orifice, the Clausing factor for orifice geometry, molecular cross-section (σ), which control ionization efficiency, and detector efficiency are included in the general relationship

$$P_i = KI^+T/\sigma D\Delta E$$

where P_i is the partial pressure corresponding to the ion intensity I^+ at T K and ΔE is the voltage excess over the appearance potential. Experimental conditions need rigid control to achieve consistent results.

TABLE VI

KNUDSEN CELL MASS-SPECTROMETRIC HEATS OF FORMATION

Group No.	Reactants	Cell material	ΔH values derived
1	$CuF_{2(s)} + Cu_{(s)}$	Cu	$(CuF)_n$, $n = 1$ to 5 (*79*)
2	$BeF_{2(s)} + Cl_2$	Graphite	$BeF_{(g)}$, $BeFCl_{(g)}$ (*31*)
3	$B_2O_{3(s)} + BF_3$	Al_2O_3	B_2OF_4, $(BOF)_3$ (*85*)
4	$SiF_4 + H_2$	Al_2O_3	$SiFH_3$, SiF_2H_2, SiF_3H (*86*)
	$CaF_{2(s)} + Si_{(s)}$		SiF_2 (*78*)
5	$VF_{3(s)} + NaF_{(s)}$		$NaVF_4$, NaV_2F_7 (*200*)
6	$W_{(s)} + WF_6$	Graphite	WF_n, $n = 1$ to 5 (*116*)
	$W_{(s)} + SF_6$		WSF_2, WSF_3, WS_2F_2
	$Ag_{(s)} + UF_4 + UF_6$	Al_2O_3	UF_4, UF_5 (*118*)
7	$MnF_{2(s)} + Mn_{(s)} + F_2$	CaF_2, Al_2O_3, Pt	MnF_n, $n = 1$ to 4 (*77*)
	$ThF_4 + Ca$	Mo	ThF_3, ThF_2 (*248*)

Errors also arise from the long extrapolations of ΔG°_T or ΔH°_T to 298 K using calculated thermodynamic functions. Although values derived by this technique are never as precise as those found calorimetrically, they are often the only ones available for many species. Representative examples of the technique are given in Table VI.

Photoionization mass spectrometry, by way of contrast, is a low-temperature variant. It employs a monochromated UV source to detect accurately the onset of molecular dissociation (see Section II,A). The heats of formation of KrF_2 (*28*) and HOF (*24*) have been so measured.

Increased pressures in a mass spectrometer lead to ion–molecule reactions, and measurements of such equilibria can be used to derive heats of formation or dissociation energies of complex fluoro ions. Ion cyclotron resonance spectrometers are mainly employed (*222*).

5. *Solid-State Equilibria*

Metal–metal fluoride electrodes can be connected by calcium fluoride crystal discs which function as solid electrolytes by fluoride ion transport without any electronic conduction (*224*) (see Table VII). The

TABLE VII

SOME FLUORIDES STUDIED BY CELL METHODS

Fluoride	References
AlF_3, PbF_2, ThF_4, UF_3, NiF_2, CoF_2	*113*
Lanthanide trifluorides	*139, 183, 184*
FeF_2, CoF_2, NiF_2	*52, 209, 229*

emf of chemical displacement cells of the type

$$M,MF_n/CaF_2/M',M'F_m$$

can be measured up to 1200 K to obtain ΔG and ΔH values for the reactions

$$mM + nM'F_m \rightleftharpoons nM' + mF_n$$

The main difficulty is to prevent pyrohydrolysis over the long experimental periods. (Moisture is removed by "gettering" with hot lanthanides or actinides.) The potentials of M/MF_n reference electrodes have also been used to study activities of metals in alloys, carbides, and borides (*208*). The accuracy is limited by reproducibility of potentials (2 ± 1 mV) as a fraction of the cell potential and indeterminate errors. The latter can be avoided by checking for internal consistency (e.g., measuring emfs of two cells against a common third electrode).

Applications to complex fluorides should be possible using the more conducting solid electrolytes now available.

6. *Solution Equilibria*

The stepwise formation of fluoro complexes in aqueous solution has been extensively studied in recent years by standard techniques (*192*). The introduction of the LaF_3 electrode has enabled fluoride activities to be measured directly, even with the "insoluble" fluorides such as CaF_2 or PbF_2 (*34, 81*). Values obtained depend on the salts added to maintain constant ionic strength, and care must be taken in making comparisons since not all results are extrapolated to zero strength (*15*). Key references to work in this field can be gleaned from standard compilations of stability constants.

TABLE VIII

SOME COMPLEX FLUORIDE MELTS STUDIED MASS SPECTROMETRICALLY

Fluoride	Reference
BeF_2–NaF	*17*
BeF_2–LiF	*25*
AlF_3–NaF	*150*
GaF_3–LiF	*247*
Lanthanide trifluoride–NaF	*210*
VF_3–NaF	*211*

The stability of complex fluorides in molten salt solutions has also been widely investigated. The studies of cryolite and chiolite in NaF/AlF_3 melts by cell methods (*67*) or by mass-spectrographic examination of vapor species (*150*) are typical.

Representative references are given in Table VIII.

G. Kinetic Methods

The formal similarity between the Arrhenius rate equation $K = A \exp(-E/RT)$ and the van't Hoff equilibrium equation $K = \exp(\Delta S^\circ/R) \exp(-\Delta H/RT)$ means that the constants are related by $K = k_f/k_r$ and $\Delta S^\circ/R = \ln(A_f/A_r)$, where the subscripts refer to forward and reverse reactions. The equilibrium constant remains a ratio of rate constants, even when the normal Boltzmann distribution is perturbed. Similarly, the reaction enthalpy change is related to activation energies by $\Delta H^\circ = E_f - E_r$. Hence for some homolytic fissions the enthalpy of bond-breaking can be related directly to the activation energy of the process when the reverse reaction has zero activation. Benson discusses in detail the estimation of rate parameters and thermochemical values (*19*). The kinetics of radical addition, hydrogen abstraction, combination, and disproportionation reactions with perfluoroalkyl and difluoroamino radicals have been widely studied (*223, 235*), but rather than derive thermodynamic data for the forward reaction it is more usual to accept these data and derive parameters for the reverse reaction. Bond energies can also be derived from kinetic data by means of empirical relations between activation energies and enthalpies of the broken bonds. The Evans–Polanyi relation $E = \alpha\Delta H^\circ + \beta$, which fitted results from sodium flame reactions ($Na + RX \rightarrow NaX + R$), also holds for hydrogen abstraction reactions ($X^\cdot + RH \rightarrow HX + R$ where $X = NF_2$, CF_3, or halogen) as R is varied (*149*).

The decomposition kinetics of sulfur oxyfluorides provide simple inorganic examples. Thus the shock wave decomposition of SO_2F_2 yields $D(O_2SF—F)$ (*245*), and hence $\Delta H_f^\circ(SO_2F^\cdot)$, and the thermal decompositions of $(F_5SO)_2$ and of (F_5SO) yield $\Delta H_f^\circ(F_5SO^\cdot)$ and $\Delta H_f^\circ(F_4SO^\cdot)$ (*62*).

Numerous determinations of the heat of formation of carbon difluoride, a transient intermediate in the production of PTFE, for example, have been made. The most recent one has combined kinetic and equilibrium approaches. The equilibrium $C_2F_4 \rightleftharpoons 2CF_2$ was studied at 1150–1600 K at 0.07–46 bar in dilute argon mixtures using incident and reflected shock waves. The carbene concentration was monitored at 250 nm after a careful study of the extinction coefficient over a wide temperature range. Rate parameters were found for forward and back

TABLE IX

DISSOCIATION HEATS OF TETRAFLUOROETHYLENE[a]

Method	ΔH_r° (kJ mol^{-1})
Kinetic activation energies	295.5 ± 15
Second-law equilibrium treatment	289.5 ± 8
Third-law equilibrium treatment	287.9 ± 7
Mean	290.8 ± 5
$\Delta H_f^\circ(CF_2) = -183.9 \pm 4$ using $\Delta H_f^\circ(C_2F_4) = -658.6 \pm 3$	

[a] From Schug and Wagner (*202*).

reactions, since the activation energy of radical recombination is not zero in this example. The equilibrium concentrations of CF_2 were also measured. The results (Table IX) show the extent of agreement possible between the different approaches.

IV. Methods of Estimation

There is insufficient experimental effort available to obtain all the desirable data, and estimates are needed to fill gaps or even to help choose between discrepant values. In addition, estimated values for unknown or transient compounds can indicate rational syntheses, or possible reasons for the "nonexistence" of compounds (*64*).

Methods can be based on some preconceived concept of bonding, with ionic and covalent extremes, or on pattern recognition based on the periodic table. Miscellaneous methods of limited applicability link bond strength with other physical properties. The *a priori* calculation of heats of formation by wave mechanics is possible in theory. In practice, the most widely applied method incorporates experimental data to derive atom or bond parameters which can then be used for calculations on closely related compounds.

A. IONIC MODELS

The ionic model, developed by Born, Landé, and Lennard-Jones, enables lattice energies (U) to be summed from inverse square law interactions between spherically symmetrical charge distributions and interactions following higher inverse power laws. Formation enthalpies are related to calculated lattice energies in the familiar Born–Haber cycle. For an alkali fluoride

$$-\Delta H_f^\circ(MF_{(s)}) = U_{MF} - \Delta H_f^\circ(M^+_{(g)}) + \Delta H_f^\circ(F^-_{(g)})$$

The early agreement between calculated and experimental heats for fluorides was fortuitous because the high value given to $D(F_2)$ was compensated by the large electron affinity value $[\Delta H_f^\circ(F^-_{(g)}) = \frac{1}{2}D(F_2) - EA(F)]$. The drop in value of $\Delta H_f^\circ(F^-_{(g)})$ over the years (see Table I) vitiates some of the more elaborate lattice-energy calculations and Kapustinskii's semiempirical method seems adequate (*138*), but see reference (*126*).

A certain amount of covalence can be tolerated in the model because the Madelung part of the lattice energy $Mz_1z_2e^2/r$ is self-compensating. Here, as covalence increases, nonintegral charges z_1 and z_2 are compensated by a shorter internuclear distance (r) than the ionic radii sum. Garrick's ionic model for covalent halides introduces a similar compensation (*96*). Neglect of close-range repulsions is compensated by effectively reducing Coulombic interactions by using ionic radii which yield shorter-than-actual bond lengths. Further terms allowed for moments induced by the central cation polarizing surrounding anions. Some of his calculated values for the reaction heats for

$$M^{n+}_{(g)} + nF^-_{(g)} \rightarrow MF_{n(g)}$$

are compared with experimental values in Table X. These are only order-of-magnitude calculations for standard enthalpies, because of the overwhelming contribution from ionization energies. Pearson allows for van der Waals interactions in his model using virial coefficient data obtained from inert gases isoelectronic with ions. In a polarizable ion model, a rather complex function of polarizability allowed for covalence (*176*). Standard formation enthalpies cannot be estimated to much better than 100 kJ.

The charge distribution in complex fluoroanions is more difficult to treat. An overall thermochemical radius can be assigned by inverting the Kapustinskii method (*138*), but more recent energy minimization calculations have claimed to arrive at charge distributions (*125*).

TABLE X

HEATS OF FORMATION (kJ mol^{-1}) RELATIVE TO GAS-PHASE IONS (*96*)

	Calculated (1) for 0 K	Experimental (2) at 298 K	(1)/(2)	(1) − (2)
BF_3	7,991	7,811	1.02	180
AlF_3	6,109	5,910	1.03	199
CF_4	13,347	14,908	0.90	1,561
SiF_4	12,301	10,991	1.12	1,310
GeF_4	10,125	10,519	0.96	394
PF_5	18,368	16,678	1.10	1,690

B. ELECTRONEGATIVITY METHODS

Heats of formation can be derived by reversing the Pauling definition of electronegativity, but empirical corrections are needed to allow for extra strength of multiple oxygen or nitrogen bonding, as in

$$-\Delta H_f^\circ = 96.5 \sum_{A-B} (\chi_B - \chi_A)^2 - 55.4n_N - 26.0n_O$$

where χ_B and χ_A are atom electronegativities, n_N and n_O the number of nitrogen and oxygen atoms. Wilcox and Bromley (*236*) have carried this method to its logical conclusion by data-fitting to known heats. Additional parameters Y and W do not have any physical significance in

$$-\Delta H_f^\circ = n_{AB}(\chi_B - \chi_A)^2 + n_A Y_A + n_B Y_B + n_{AB}(W_B/W_A)$$

but are adjustable fitting parameters. The average deviation from experiment with 26 fluorides was 16 kJ mol^{-1}. The value they predicted for $\Delta H_f^\circ(\text{BiF}_3)$ was 142 kJ less than a later experimental value.

Sanderson (*198*) combines the above approaches in a more reasoned empirical procedure. He argues that electronegativity is an atomic property and derives values from the relative compactness of atoms. When atoms of different kinds combine, the electronegativities equalize by transfer of electron density and consequent creation of partial nonintegral charges. The fractional ionic content of the molecule is calculated from the charge created. The covalent bonding in homonuclear species is partly replaced by ionic bonding in heteronuclear ones, and not supplemented by it as in Pauling's concept. A small admixture of ionic bonding produces a disproportionate increase in total bonding energy. The atomization energy E of a molecular fluoride is given by

$$E = t_i(1389/r_0) + (1 - t_i)(E_{AA}E_{BB})^{1/2}(r_C/r_0)$$

where t_i and $(1 - t_i)$ are ionic and covalent fractions, r_0 the actual bond length, and r_C the sum of the covalent radii. E_{AA} and E_{BB} are homonuclear single-bond energies. (The numerical constant is appropriate to energies in kilojoules and distances in angstroms.)

For nonmolecular solids, called coordinated polymers, he substitutes the Madelung part of the lattice energy

$$E = t_i f \cdot M(1389/r_0)K + n(1 - t_i)(E_{AA}E_{BB})^{1/2}(r_C/r_0)$$

where M is the Madelung constant, K the repulsion coefficient more usually expressed as $(1 - 0.345/r_+ + r_-)$, $f = 1$ for univalent ions, and n represents the number of covalent bonds formed by the electron pairs available to the cation, which is not necessarily the crystal coordination number. (In practice, f and n are used as adjustable parameters.)

The procedure does involve circular arguments because some homonuclear bond energies (E_{XX}) are derived from known enthalpies of series of compounds and others by fitting a linear relation $E_{XX} = CrS$ where S is the Sanderson electronegativity and C is a constant related to period number. For example, in the second period the single-bond energy for Be is interpolated and those for N, O, and F extrapolated. The last three are regarded as unweakened bond energies compared with the fully weakened values found in $D(H_2N{-}NH_2)$, $D(HO{-}OH)$, and $D(F{-}F)$, respectively. An intermediate set of partially weakened values are also used. The bond weakening effect lessens as the groups are descended, but still persists in homonuclear single bonds of Sb, Te, and I. Sanderson takes an unconventional view in regarding bond-

TABLE XI

HEATS OF ATOMIZATION (kcal mol^{-1}) OF MONOFLUORIDES BY SANDERSON'S METHOD[a]

Fluoride	Partial charges on each atom	Calculated	Experimental	Difference
$O'F'$	0.05	46.4	52.6	−6.2
$Cl'F'$	0.09	62.4	60.0	2.4
$Br'F'$	0.13	62.9	58.8	4.1
$N'F'$	0.14	71.8	80.7 (or 73.3)	−8.1
AsF'''	0.20	104.1	96.9	7.2
$I'F'$	0.21	67.9	66.4	1.5
CF''	0.22	125.2	130.8	−5.6
GeF'''	0.24	106.9	115.3	−8.4
HF'	0.25	142.0	135.3	6.7
BF'''	0.33	156.2	180.1	−23.9
SiF'''	0.34	129.2	128.4	0.8
CuF'''	0.38	97.7	101.9	−4.2
AgF'	0.38	80.6	83.9	−3.3
PbF'	0.41	83.6	83.9	−0.3
AlF'''	0.44	134.8	158.9	−24.1
BeF'	0.47	142.7	144.1 (or 134.9)	−1.4
MgF'	0.55	123.9	109.5	14.4
TiF'''	0.58	103.0	105.4	−2.4
CaF''	0.62	127.7	126.4	1.3
SrF'''	0.66	130.7	128.7	2.0
BaF'''	0.73	129.5	139.5	−10.0
LiF'	0.74	168.9	136.3	32.6
RbF'	0.86	129.7	115.0	14.7
CsF'	0.90	129.5	118.8	−10.7

[a] Calculated values are derived from data at 298 K. The experimental values are D_0° figures. F′ indicates use of the fully weakened covalent single bond energy, F‴ the unweakened bond energy.

weakening as an intraatomic effect because bond energies of HF, H_2O, and NH_3 are reproduced using the fully weakened covalent energies. Lone-pair repulsions, which could give interatomic effects, are absent in these molecules.

The validity of the method was rechecked with data from Herzberg's recent compilation on gaseous diatomics (*121*) (Table XI). Calculated heats of solid halides are in better agreement with experimental values. In some molecules the use of more than one value of fluorine bond energy is required to reproduce experimental heats. Thus PF_5 or AsF_5 require two fully weakened values and three unweakened values, which is sensible on chemical and structural grounds.

The method has been confined to main-group compounds presumably because of irregularities expected with unsymmetrical charge distributions in transition metal ions. The noble gas compounds remain outside the scope of the method because of the way in which electronegativity is defined (atom compactness relative to interpolated noble atom compactness). The main weakness of the method when applied to fluorides is in the somewhat arbitrary choice of fluorine bond energies.

C. COVALENT MODELS

In this type of method it is assumed that constant bond properties are transferable between molecules. More sophisticated versions extend the bond property over nonadjacent atoms, and group properties, rather than those of bond pairs, are transferred. In the extreme, a summation of interactions scheme can be devised rather like a lattice energy summation. These methods, mainly applied to organic compounds and recently to inorganic clusters (*120*), are summarized by Cox and Pilcher (*61*). The group additivity method of Benson transfers sets of bond energies with identical next nearest neighbors, while making allowances for special interactions (*19*). Bond polarity can be taken into account using electronegativity concepts (*22*). The theoretical soundness of these bond energy schemes is questionable because the bond dissociation energy is measured with respect to ground-state gas atoms, whereas in compounds the atoms are in their valence states. The intrinsic bond energy should include the atom reorganization energy. (The zero-point energies are also included in dissociation energies at 0 K, but since they are additive functions they can be incorporated into atomization heats at 298 K). The consequence of neglecting reorganization energies is seen in the apparent irregularities between bond energies as atoms are removed in succession from a molecule (see Section V,A). Unfortunately, intrinsic bond energies cannot be determined by experiment, or computed reliably, since actual valence states are multiconfigurational. Also, simple bond energies are not strictly transferable as shown by heat changes in redistribution reactions. For example, the formation of mixed ternary compounds from simple binaries is rarely athermal (see Section V,B).

D. RELATION OF BOND ENERGIES TO OTHER MOLECULAR PROPERTIES

1. *Molecular Volume*

Intuitively, one would expect a volume contraction on forming a strongly bonded compound from the elements. Indeed, Richards (*190, 191*) regarded heats of formation as heats of compression. The fractional volume contraction, ΔV = (molecular volume − Σ atomic volume)/Σ(atomic volume), has been related to formation heats for NaCl or CsCl type structures (*151*). Even nonpolar compounds in the condensed state cohere in close-packed arrays. The packing density of difluorine, derived from the ratio of the van der Waals envelope to the molecular volume, is especially low, and a larger contraction would be expected for fluorides than for other halides. This approach has yet to be systematically examined.

A more direct link with molecular volumes holds for alkali halides, because the lattice energy (U) is inversely proportional to interatomic distance or the cube root of molecular volume (MV). The latter has been approximated by a logarithmic function which gives a superior data fit. Plots of ΔH_f° against log(MV) are linear for alkali halides (*37a*). Presumably, U and ΔH_f° can be equated because $\Delta H_f^\circ(M^+_{(g)})$ is a constant in a series, and ΔH_f° (halide$^-_{(g)}$) is approximately constant when the anion is referred to the dihalogen as the standard state.

TABLE XII

PACKING DENSITIES OF SOLID ELEMENTS[a]

Group V		Group VI		Group VII	
N_2	0.59	O_2	0.60	F_2	0.56
		S_8	0.77	Cl_2	0.74
				Br_2	0.75
				I_2	0.76

[a] Value expected for ordered close packing of spheres = 0.74; value expected for random close packing of spheres = 0.67

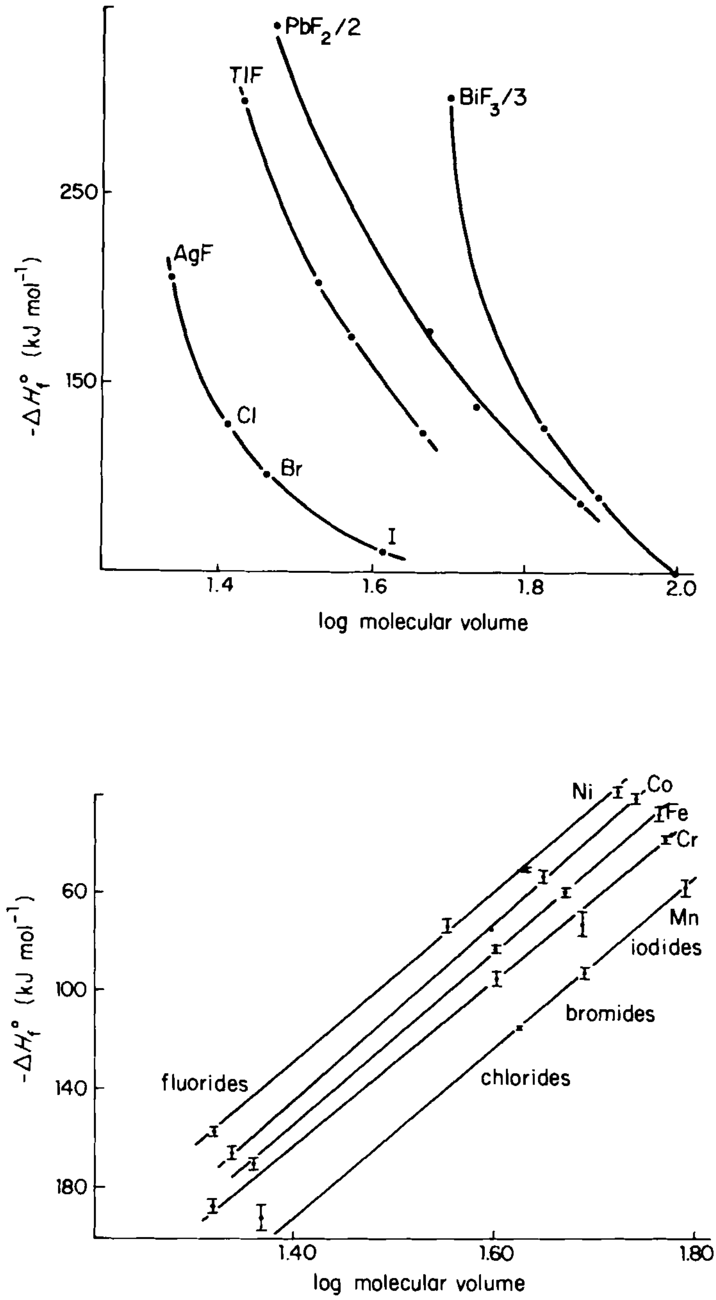


FIG. 1. Heats of formation of fluorides as a function of molecular volume.

Extension of the method to nonisostructural metal halides, some of which yield erroneous ΔH_f° values via Born–Haber cycles, is shown in Fig. 1. All curves are nonlinear with the bow increasing in the expected order Tl(I) < Pb(II) < Bi(III) < Ag(I). For the first transition metal dihalides, however, straight lines can be drawn within the limits of enthalpy errors except for Zn(II) or Mn(II) salts. Thus heats of formation of the fluorides can be extrapolated linearly from the other three halides to a first approximation.

2. *Fundamental Frequencies*

Stretching force constants K_e can be derived from fundamental frequencies, assuming a valence force field. They are also related to Morse or Linnett type equations for the potential energy (V) of a diatomic molecule, because $d^2V/dr^2 = K_e$ and $dV/dr = 0$ at the equilibrium separation r_e. Hence K_e, r_e, and dissociation energy D should be interrelated. For example $D/K_e r_e^2$ is sometimes a constant for a closely related set of molecules (*157*). However, individual bond properties (K_e and r_e) bear no general relationship to bond dissociation energies because they are different functions of (V). Smyl and Mamotov's tabulation of force constants for binary fluorides make this clear (*214a*). Their remark that "relating K_e's to bond energies should be treated with caution, particularly for molecules exhibiting a larger percentage of ionic bonding, since the magnitude of K_e is primarily a reflection of only the covalent character of a particular bond," is also too general a statement. For the hydrogen halide series, K_e is more closely related to the ionic contribution, and $D/K_e r_e$ is almost constant.

Vague statements about relations between K_e and D even for mono-

TABLE XIII

RELATION OF FORCE CONSTANT (K_e) TO IONIC PART OF BOND ENERGY (D) FOR HYDROGEN HALIDES

	HF	HCl	HBr	HI
K_e/Nm^{-1}	989	516	405	308
D(HX) (kcal mol^{-1})	136	103	87.5	71
Ionic contribution[a] (kcal mol^{-1})	98.5	56.0	42.3	27.7
Fractional ionic character[b]	0.83	0.45	0.37	0.25
$DK_e^{-1}r_e^{-1}$	0.150	0.157	0.153	0.143

[a] Calculated by Sanderson's method (*198*).

[b] Calculated assuming covalent and ionic contributions to bonding are in the ratio $1/\lambda^2$ of the charge derived from dipole moments (*152*).

valent fluorides have no quantitative significance. Inverse power relations for r_e and D hold for closely related series.

A relation between heats of formation of inorganic halides and characteristic infrared frequencies (ν) of the solids has been claimed (*156*):

$$\Delta H_f^\circ = Nh(\Sigma\nu_{(\text{products})} - \Sigma\nu_{(\text{reactants})})$$

However, the obscure choice of frequencies in the visible and UV regions in the original calculations may have been guided by a desire to fit experimental heats. In fact, the Debye rotational and translational crystal frequencies relate to sublimation energies of the lattice, and, together with internal molecular vibrations, can be used to calculate thermodynamic functions (*16*). An indirect connection between maximum lattice frequencies (ν_m) and heats of formation may hold because the former is inversely related to interatomic dimensions (see Section IV,D,1):

$$\nu_m = c(9N/4\pi V)^{1/3}$$

where N is Avogadro's constant, and V is the molecular volume. Obviously it is easier to obtain molecular volumes than Debye frequencies.

E. PERIODIC PATTERNS

A general survey has been given by Long (*158*), who points out that enthalpy regularities would only be expected over restricted areas of the periodic table. Discontinuities would be expected where an increase in coordination number occurred between Periods 4 and 5, or where the relative stability of valence states changed, or where ion configurations were stabilized. Examples of trends in mean bond energies are presented in Section V,C.

Prikhod'ko's system of unpolarized ionic radii is typical of methods based on periodic variations (*181*). He uses the relation log $R_u = f(n)$, where R_u values are univalent ionic radii (viz. Pauling) and n the number of outermost electrons. The slope of these curves enables radii for species of intermediate charge, R_u^z, or none, R_u^0, to be interpolated (Fig. 2). The approach is reminiscent of Sanderson's treatment (*198*) because the slopes, which represent the change in radius for a unit charge variation, are linear functions of electronegativities along groups and periods. Sanderson equates a unit charge transfer with $2.08\sqrt{S}$ using his electronegativity values (S) derived from compactness of atoms. Properties of fluorides were linearly related to those of other halides by plotting as functions of R_u^z sums or ratios. For example, with alkali hal-

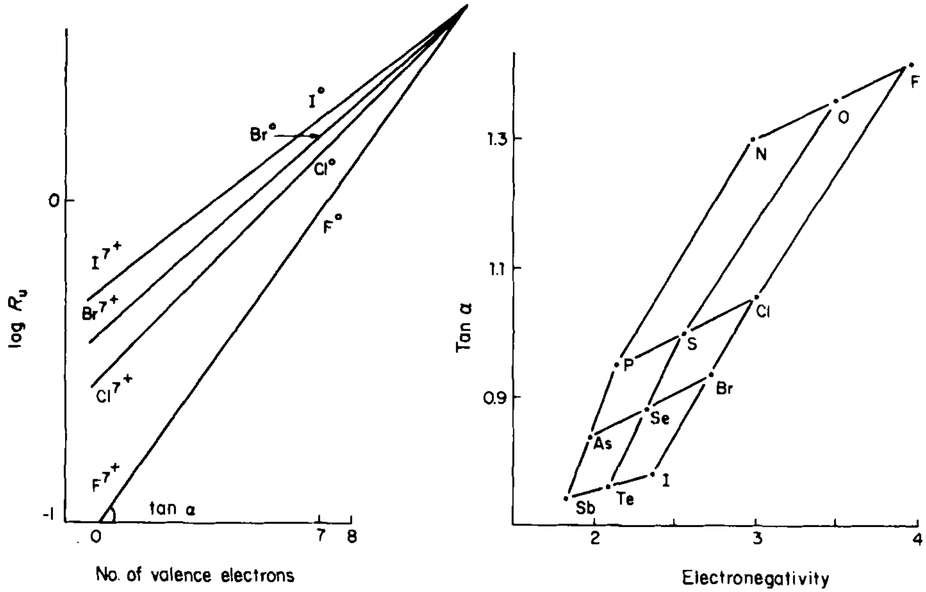


FIG. 2. Ionic radius-to-charge ratios as a function of electronegativity.

ides the effective charge on the ions was obtained by varying Δe, the charge transferred between atoms, to fit the equations

$$R_A^{Z,A} + R_B^{Z,B} = d_{AB} \qquad Z_{\min},A = -Z_{\min},B$$

$$\log R_A^{Z,A} = \log R_A^0 - m_A\left(Z_{\min},A + \frac{\Delta e}{2}\right)$$

$$\log R_B^{Z,B} = \log R_B^0 - m_B\left(Z_{\min},B + \frac{\Delta e}{2}\right)$$

where d_{AB} is the interatomic distance and m_i the radius–charge slope for species i.

The atomization energies were linearly related to the effective radius ratios $R_B^{Z,B}/R_A^{Z,|A}$. Similar relations held among Group IIIB monohalides. Linear patterns between entropies of solid halides of Period 5 and the neutral radius sum ($R_A^0 + R_B^0$) were also established.

F. ISOELECTRONIC HEATS OF FORMATION

The physical, and often the chemical, properties of isoelectronic molecules are closely related (*23*). The isoelectronic principle can be extended to a comparison of fluoro with isostructural hydroxo com-

TABLE XIV

ENTHALPIES OF FORMATION (kJ mol^{-1}) OF H_2O AND HF IN DIFFERENT PHASES

	Gas	Liquid	Solid
H_2O	−241.8	−285.85	−291.6
HF	−273.3	−303.55	−307.5
(H_2O—HF)	31.5	17.7	15.9

pounds. It is well known that F and OH are interchangeable between wide limits in many minerals and that the "fluoride-specific" lanthanum trifluoride electrode also responds to hydroxyl ions. The heats of formation of ionic fluorosulfates were found to be almost identical with those of the corresponding hydrogen sulfates, more logically named as hydroxosulfates (*187*). It seemed likely that this isoelectronic constancy was not an isolated phenomenon. Benson refers to F and OH as a homothermal pair. According to him the replacement of OH by F in a compound can increase ΔH_f° when a very electronegative element is attached or vice versa (*20*). Woolf (*243*) associated these comparatively small variations with alterations in hydrogen bonding. Replacement of OH by F reduces hydrogen bonding, which is initially much greater when OH is close to a highly electronegative entity. Dipolar aggregation must also play a part. Hence care must be exercised when making comparisons especially between extreme compounds such as H_2O and HF.

Gaseous HF remains polymerized, unlike water vapor. In the liquid

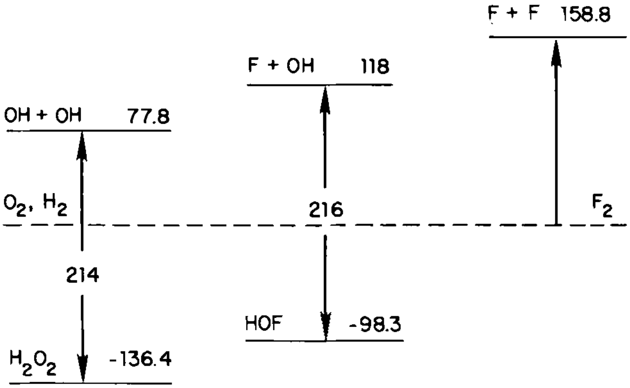
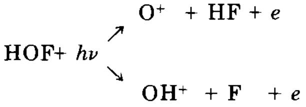


FIG. 3. Dissociation energies of H_2O_2 and Hf (kJ mol^{-1}).

or solid the difference is narrowed; the lesser polymerization which is likely with two-dimensional F—H—F bonding compared with the three-dimensional network in water, is more than compensated by the greater strength of hydrogen-bonded fluorines (Table XIV).

A simpler comparison is possible between gaseous H_2O_2 and HOF (Fig. 3). The latter has been regarded as a hydroxofluoride (*241*) whose enthalpy has been estimated indirectly by photoionization mass spectrometry (*24*).



Although ΔH_f°(HOF) is less than that of H_2O_2, the heats of dissociation to isoelectronic radicals are equal within experimental error. A direct comparison of F_2 and H_2O_2 is not possible because the arbitrary zero level is not eliminated, a point usually ignored when making comparisons along the isoelectronic series CH_3—CH_3, H_2N—NH_2, HO—OH, F—F. The comparison can be extended beyond ionic fluorosulfates to the neighboring covalent oxyacids and derivatives as shown in Table XV. It is possible to predict from the pattern of values that $\Delta H_f^\circ(AsOF_3) = -870$ kJ mol^{-1}. Recent measurements show that SO_2ClF and HSO_3Cl constitute another isoelectronic pair (Table XVI) (*50*).

Extensions to Period 5 oxyacid sequences must await enthalpy mea-

TABLE XV

HEATS OF FORMATION (kJ mol^{-1}) OF ISOELECTRIC LIQUID FLUORIDES AND OXOACIDS

Group V	ΔH_f	Group VI	ΔH_f	Group VII	ΔH_f
$OP(OH)_3$	−1274				
$OP(OH)_2F$	—	$O_2S(OH)_2$	−814		
$OP(OH)_2F_2$	—	$O_2S(OH)F$	−798	$O_3Cl(OH)$	−40.6
OPF_3	−1255	O_2SF_2	−789	O_3ClF	−23[a]
$OAs(OH)_3$	−900				
$OAs(OH)_2F$	—	$O_2Se(OH)_2$	−515		
$OAs(OH)F_2$	—	$O_2Se(OH)F$	−523[b]	$O_3Br(OH)$	103[c]
$OAsF_3$	—	O_2SeF_2	−494[b]	O_3BrF	109[d]

[a] From Cartwright and Woolf (*51*).
[b] Unpublished measurements.
[c] Estimated from $\Sigma\,\Delta H_f^\circ(HClO_4 + KClO_4 - KBrO_4)$.
[d] From Johnson *et al.* (*131*).

TABLE XVI

COMPARISON OF HEATS OF FORMATION (kJ mol^{-1}) OF SULFURYL HALIDES WITH HALOSULFURIC ACIDS

	Gas	Liquid		Gas	Liquid
SO_2F_2	−769.7	−788.5	SO_2ClF	−564.0	−589.8
	6.9	9.2		5.8	9.1
HSO_3F	−762.8	−797.7	HSO_3Cl	−558.2	−597.5

surements. These are likely to show wider variations because octahedral coordination allows more extended series and greater hydrogen-bonding possibilities.

The hydroxo species isoelectronic with a fluoride does not always exist in the vapor, but its enthalpy can be estimated by summing heats of the component oxides:

$$OCF_2\text{: } 636 \qquad OC(OH)_2 \equiv O_2C + H_2O = 636 \text{ kJ mol}^{-1}$$

$$OSF_2\text{: } 548 \qquad OS(OH)_2 \equiv O_2S + H_2O = 540 \text{ kJ mol}^{-1}$$

Again, this can be generalized because, as other workers have discovered, enthalpies of most solid hydroxides are equal to the sum of the component oxide heats. For example, Van My noted that many dehydration heats were between 40 and 60 kJ mol^{-1} and proposed (*227*)

$$\Delta H_f^\circ[X(H_2O)_n] - \Delta H_f^\circ(X_{(s)}) = n\Delta H_f^\circ(H_2O_{(g)}) - 54n$$

Reznitskii put forward a similar equation (*182*)

$$\Delta H_f^\circ(M_xO_y\cdot nH_2O_{(s)}) = \Delta H_f^\circ(M_xO_{y(s)}) - n(292 \pm 8)$$

which means that hydration of oxides is an athermal reaction in the solid state. Obviously, the relation breaks down for strong acids or alkalis formed by exothermic hydration. These are not isostructural with fluorides.

Internal consistency among enthalpy values can also be judged without estimating absolute enthalpies using the oxide summing method. Finch and co-workers (*89*) obtained the following enthalpy values (kJ mol^{-1}) for solids:

IOF_3	−555	KIF_6	−1492	$RbIF_6$	−1473
IO_2F	−240	KIO_2F_2	− 877	$RbIO_2F_2$	− 875
Δ =	309	Δ =	615	Δ =	598

The differences, as expected, are multiples of $\Delta H_f^\circ(H_2O_{(s)})$. It is possi-

TABLE XVII

ENTHALPIES (kJ mol^{-1}) OF IODINE OXYFLUORIDES

	Calculated	Experimental
IO_2F	246	246
IOF_3	555	555
IF_5	894	893

ble to calculate heats of formation of iodine pentafluoride and iodine oxyfluorides from that of iodic acid by assuming athermal solid-state reactions (Table XVII):

$$HIO_3 + nHF \rightarrow nH_2O + IO_{\frac{(5-n)}{2}}F_n$$

Fluorobromates(V) have been isolated recently (*97*). Their enthalpies can be estimated from the equivalences

$$\begin{array}{lll} KBrO_2F_2 \equiv KBrO_2(OH)_2 & \equiv KBrO_3 + & H_2O \\ \underline{KBrOF_4 \equiv KBrO(OH)_4} & \underline{\equiv KBrO_3 +} & \underline{2H_2O} \\ KBrOF_4 - KBrO_2F_2 & \equiv H_2O & \end{array}$$

The method is also applicable to organofluorides and their corresponding hydroxo analogs. Good agreement is obtained when the mean enthalpies of gas and liquid states are compared (*243*).

G. QUANTUM CALCULATIONS

Hurley, (*122*) has summarized calculations for compounds of the first-row elements. Extremely high accuracy is needed because the enthalpy is a small difference between the large electronic energies of a molecule and its constituent atoms as derived from the electronic Schrödinger equation. Discrepancies of 1–10 eV are found for the dissociation energies of simple diatomics even when the calculations are taken to the Hartree–Fock limit, because of the extensive electronic reorganization on forming molecules from atoms. Correlation energies have to be estimated. Das and Wahl have done this for difluorine and obtained a dissociation energy close to the experimental values (*29, 63*). However, such computations are not a practical proposition for larger molecules and semiempirical methods are needed. Dewar's MNDO method used 50 properties from 12 fluorine-containing molecules to obtain optimized atomic parameters for fluorine (*65*) which followed the sequence of C, N, and O parameters similarly obtained from a set of 35 molecules. The heats of formation of 71 fluorine compounds containing the other atoms were derived with a mean error of 41 kJ mol^{-1}. Poor agreement was achieved with nitrogen-containing compounds and the ONF_3 value was excluded from the average (calc. + 95.4; exptl. − 163.2 kJ mol^{-1}). The method has been extended to Period 3 elements (Si, P, S, Cl) but, because 3d AOs have not been included, the heats of formation of only a restricted range of fluorides can be calculated.

Similar MNDO|calculations for N, O, F compounds using bond parameters for O—F and N—F permitted enthalpies of unknown compounds such as $F_nN(OF)_{3-n}$ to be predicted and possible syntheses evaluated (*96*). [The input data to this set of calculations included a wrong value for $\Delta H_f(F_{(g)}) = 270.3$ kJ mol^{-1}. It should be noted that experimental heats of formation of atoms are needed in all these calculations.]

Ab initio calculations may be applied to isomerization reactions or "bond separation reactions" in which the bond type persists and correlation energies are unlikely to alter. For example,

$$F_2NOF + 2NH_3 + H_2O \rightarrow H_2NOH + 2FNH_2 + HOF$$

The value of $\Delta H_f^\circ(F_2NOF)$ derived from bond separation energies of this reaction was 55.7 kJ mol^{-1}. This compared with the empirical MNDO calculation of − 85.8 kJ mol^{-1} (*172*).

At the present time, semiempirical quantum calculations applied to a restricted range of fluorine compounds cannot be said to be more successful than other empirical methods, such as Sanderson's, although they yield other molecular properties in addition to enthalpies.

V. Trends in Heats

Three trends are of special interest. First, the variation of bond strength with formal oxidation state. A regular enhancement of strength with lowering of oxidation state might be expected in line with an increasing bond ionicity. However, irregularities could occur with change in molecular shape and the accompanying bond rehybridization. Regular geometries appear in even-electron molecules and distorted geometries in odd-electron molecules of main-group (A) elements. The d electrons from transition elements also cause distortions to VSEPR geometries, according to Burdett (*39*), when they occupy the highest orbital levels unsymmetrically—e.g., low oxidation states of Group V, VI, and VIIB fluorides. Hence the alternations which occur between odd and even fluoride molecules of Group A elements will not be followed by fluorides of Group B elements. Enhanced stabilities might also be met at stable half-filled or filled-shell configurations.

Second, the effect of substituting fluorine by other atoms or groups

TABLE XVIII

VARIATION OF BOND ENERGY WITH OXIDATION STATE OF GROUP II, III, AND IV FLUORIDES

	$-\Delta H^\circ_{f(g)}$	$\bar{D}$	$D(\mathrm{MF}_n\text{—F})$[a]		$-\Delta H^\circ_{f(g)}$	$\bar{D}$	$D(\mathrm{MF}_n\text{—F})$
BeF_2[b]	796	641	672	CuF_2[c]	267	383	351
BeF	203	610	610	CuF	−4.6	414	414
BF_3[d]	1136	643	643	AlF_3[e]	1213	592	543
BF_2	581	648	543	AlF_2	749	617	566
BF	117	752	752	AlF	262	667	667
				NdF_3[f]	1271	610	690
				NdF_2	660	570	596
				NdF	144	544	544
CF_4[g]	933	491	520	SiF_4[h]	1615	596	605
CF_3	488	480	383	SiF_3	1085	591	571
CF_2	184	529	526	SiF_2	588	599	638
CF	−255	539	539	SiF	19	549	549
GeF_4[i]	1190	471	518	TiF_4[j]	1552	585	467
GeF_3	751	455	257	TiF_3	1164	625	590
GeF_2	573	554	626	TiF_2	653	642	341
GeF	26	482	482	TiF	391	942	942
SnF_4[k]	1024	411	471	PbF_4[k]	828	335	397
SnF_3	632	391	226	PbF_3	510	314	157
SnF_2	485	473	478	PbF_2	432	393	431
SnF	86	467	467	PbF	80	354	354

[a] $\bar{D}$ is the average energy per bond and D is the energy to remove the first fluorine atom in kJ mol^{-1}.

[b] From Sanderson (*198*).

[c] From Ehlert and Wang (*79*).

[d] From Higgins *et al.* (*114*) and Srivastava and Farber (*215*).

[e] From JANAF Tables (*123*).

[f] $\Delta H^\circ_f(\mathrm{Nd}_{(g)}) = 321$ kJ (*249*).

[g] From Schug and Wagner (*202*).

[h] From Farber *et al.* (*87*) and Wang *et al.* (*233*).

[i] From Adams *et al.* (*1, 3, 5*) and Bennett *et al.* (*18*).

[j] From Hastie *et al.* (*111*).

[k] From Bennett *et al.* (*18*).

on heats of formation can be used to test transferability of bond energies and hence the reliability of estimating heats, assuming its validity. Third, interelement relations will show up in periodic variations which reveal discontinuities associated with periodic structure.

The precision of heats of formation obtained on transient high-temperature fluorides by mass-spectrometric methods is much less than that obtained on fluorides which are stable at room temperature, by fluorine bomb calorimetry for example. One incorrect heat can affect neighboring heats in a series and alter a sequence. Hence only major irregularities in series should be taken as significant.

A. BOND STRENGTHS AND OXIDATION STATE

Some of the few complete sets of enthalpies for binary fluorides are collected in Tables XVIII and XIX. The inversion in dissociation heats for copper and beryllium fluorides can be associated with the closed-shell configurations of Be^{2+} and Cu^+. The alternations in bond energies

TABLE XIX

VARIATION OF BOND ENERGY WITH OXIDATION STATE OF GROUP V, VI, VII, AND VIII FLUORIDES

	$-\Delta H^\circ_{f(g)}$	$\bar{D}$	$D(MF_n—F)$		$-\Delta H^\circ_{f(g)}$	$\bar{D}$	$D(MF_n—F)$
NF_3[a]	133.5	282	246	MoF_6[b]	1559	449	397
NF_2	−33	300	304	MoF_5	1241	459	367
NF	−257	295	295	MoF_4	954	482	441
SF_6[c]	1221	329	326	MoF_3	592	496	503
SF_5	971	329	301	MoF_2	168	492	519
SF_4	782	337	347	MoF	−272	466	466
SF_3	481	333	264	WF_6[d]	1722	508	404
SF_2	217	327	352	WF_5	1397	528	447
SF	−13	343	343	WF_4	1029	549	577
XeF_6^+[e]	−839	135	36	WF_3	531	539	505
XeF_5^+	−795	154	242	WF_2	105	556	544
XeF_4^+	−958	133	43	WF	−360	567	567
XeF_3^+	−922	162	204	CrF_3[f]	660	432	525
XeF_2^+	−1029	150	53	CrF_2	216	386	316
XeF^+	−1003	247	247	CrF	−21	456	456
FeF_3[f]	785	480	514	MnF_3[g]	779	434	335
FeF_2	350	463	473	MnF_2	525	484	526
FeF	−43	453	453	MnF	78	442	442
$Cr_{(g)}$	397.5						
$Mn_{(g)}$	284.5						
$Fe_{(g)}$	417.1						

[a] From Evans and Tschuikow-Roux (*82*).

[b] From Hildenbrand (*117*), Kleinschmidt *et al.* (*147*), and Nuttall *et al.* (*166*).

[c] From Benson (*20*), Bott and Jacobs (*35*), Hildenbrand (*155*), and Vaughan and Muetterties (*228*).

[d] From Dittmer *et al.* (*70*) and Hildenbrand (*116*).

[e] From Berkowitz *et al.* (*26*).

[f] From Zmbov and Margrave (*250*).

[g] From Ehlert and Hsia (*77*) and Zmbov and Margrave (*250*).

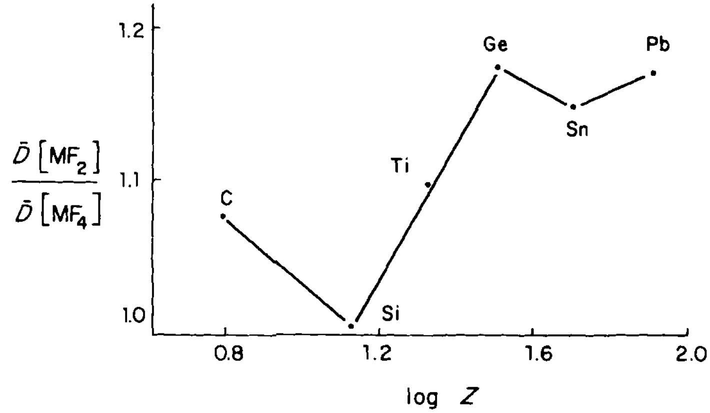


FIG. 4. Relative stabilities of Group IV fluoride oxidation states.

for Group III and IVA fluorides show the weakening effect of odd electron species. (Aluminum difluoride seems exceptional, but there is a large uncertainty in its formation heat.) Carbon monofluoride is exceptionally strong, as confirmed by the C—F distances which are inversely related to bond strength (C—F distances in CF = 127, CF_2 = 130, and CF_4 = 132 pm, compared with Si—F distances in SiF = 160, SiF_2 = 149, and SiF_4 = 154 pm). The irregularity at $D(AF_2—F)$ in the Group IV series can be associated with the hybridization change from pyramidal to planar geometry. This change is smaller for silicon than for carbon fluorides in conformity with the dissociation energies. Lower down the group the increasing stability of the divalent state surprisingly peaks at germanium (Fig. 4). The titanium fluoride sequence is different in that the odd-electron molecule, TiF_3, is at a maximum in dissociation energy rather than at the minima encountered with Group IVA trifluorides. The difference is probably linked with the fact that TiF_3, as shown by the ESR matrix method, is planar with the odd electron located in an sd_z^2 hybrid orbital. The Group IVA trifluorides are pyramidal.

Lanthanide fluoride sequences show monotonic increase in bond energy with increasing oxidation state, although one would expect a maximum for EuF_2 in the europium series at the stable f^7 configuration.

The nitrogen fluoride series has an unexpected maximum at NF_2 but the sulfur fluorides show alternations in $D(SF_n—F)$ values with minima at odd-electron molecules. If rehybridization energies at $D(SF_4—F)$ and $D(SF_2—F)$ stages are superimposed on the regular

TABLE XX

BOND ENERGIES IN S—N—F COMPOUNDS[a]

	D(S—F) (kJ mol^{-1})
NS—F	383 ± 25
NSF—F	151 ± 29
NSF_2—F	318 ± 29

[a] From O'Hare *et al.* (*171*).

bond strength sequence for even-electron molecules, $D(SF_5—F) < D(SF_3—F) < D(SF—F)$, the observed sequence $D(SF_5—F) > D(SF_4—F) < D(SF_3—F) > D(SF_2—F) < D(SF—F) > D(S—F)$ is explicable. [Hildenbrand's enthalpy value for SF_2 (*115*) is out of line with Benson's value (*19*) and Sanderson's estimate (*198*), possibly because a wrong sign has been taken for the reaction heat $S + SF_2 \rightarrow 2SF$.]

The mean bond energy $\bar{D}(S—F)$ for SF_6 can be regarded as a single bond energy and its transferability to ternary compounds can be examined in S—N—F compounds (see Table XX).

Only the thiazyl trifluoride can be said to have a single S—F bond within the error limits. The stronger bond in the monofluoride accords with a bond order of 2.4 for S—N estimated from a force constant–distance relationship. The odd-electron molecule NSF_2 has the weakest bond.

A complete set of tungsten fluoride values obtained from a Knudsen effusion study of WF_6 + W reactions (*116*), and from tungsten transport in fluorine-containing gases (*70*), allows transition-metal and main-group element sequences to be compared. There is no alternating pattern in bond energies, but the increase above the rising trend with lower oxidation state which occurs at $D(WF_3—F)$ may indicate a favorable bond rehybridization energy. However, the pattern for molybdenum fluorides is different and peaks at D(MoF—F) (*117*). Some incomplete sequences have been determined for transition-metal fluorides by Knudsen cell effusion methods. There is considerable discrepancy between different workers' figures, and attempts to connect dissociation energies with d-electron count must remain tentative. For Cr and Mn, the minimum energy corresponds to the configurational change $d^4 \rightarrow d^5$, and a similar minimum would be predicted for $D(FeF_3—F)$ in the iron fluoride series. The bond dissociation energies, apart from the above irregularities, appear to increase with oxidation state as opposed to the decrease with the titanium series. Further knowledge of gas-phase structures is needed for any adequate explanation.

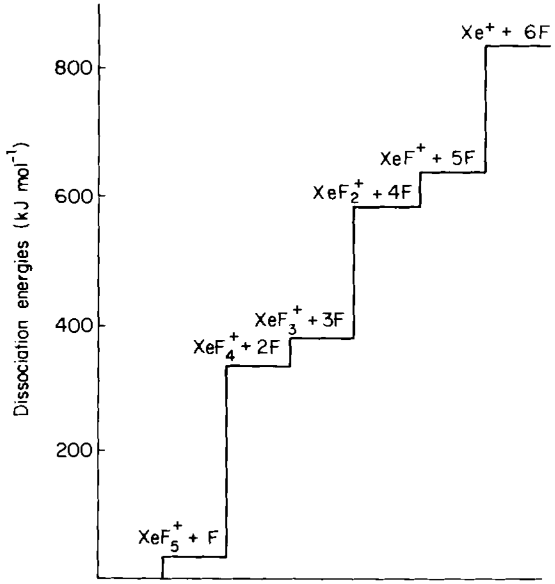


FIG. 5. Stepwise dissociation energies for the xenon hexafluoride cation.

Heats of formation for a complete set of Group VIIA fluorides are unavailable, but a set of xenon fluoride cations, isoelectronic with iodine fluorides, exhibits the alternating pattern expected for odd- and even-electron molecules. The original energy-level diagram for stepwise fluorine dissociation is shown in Fig. 5. The tabulated values were derived from the ionization energies of XeF_n and the threshold values for $XeF_n^+ \rightarrow XeF_{n-1}^+ + F$, where n is even (*27*), together with heats of formation obtained by reaction calorimetry (*137*).

B. Additivity in Ternary Compounds

Following Sanderson's reasoning (*198*), replacement of fluorine by another element or group reduces the overall electronegativity of the molecule. The ionicity of the fluorine bonds decreases while the ionicity of other bonds will generally increase relative to those in binary compounds. The changes on substitution should parallel electronegativity changes. However, it is not possible to generalize as to the extent or direction of deviation of ternary atomization energies compared with means from binary energies because of the number of factors involved.

The heats of substituted Group IVA fluorides (Table XXI) illustrate these points. All the substituted carbon fluorides are less stable than calculated from additivity, with destabilization increasing roughly

TABLE XXI

"ADDITIVITY" IN SUBSTITUTED GROUP IV AND VA FLUORIDES

$-\Delta H^\circ_{f(g)}$ (kJ mol^{-1})

	Expt. (E)	Calc. (C)	(E) − (C)		(E)	(C)	(E) − (C)
CF_4[a]	933			SiF_4[b]	1615		
CF_3H	698	719	−21	SiF_3H	1226	1203	23
CF_2H_2	449	504	−55	SiF_2H_2	804	791	13
CFH_3	230	290	−60	$SiFH_3$	416	380	36
CH_4	75			SiH_4	−33		
				CF_4[c]	933		
CF_3Cl[a]	695	724	−29	CF_3NF_2	455	466	−11
CF_2Cl_2	481	515	−34	$CF(NF_2)_2$	200	233	−33
$CFCl_3$	276	305	−29	$C(NF_2)_4$	−2		
CCl_4	96						
				NF_3[d]	133.5		
				NF_2H	65	104	−39
				NFH_2	38	75	−37
				NH_3	46		

[a] From Cox and Pilcher (*61*).

[b] From Farber and Srivastava (*86*).

[c] From Sinke *et al.* (*213*).

[d] $\Delta H_f^\circ(NFH_2)$ assumed equal to $\Delta H_f^\circ(NH_2OH)$ (*19, 246*); $\Delta H_f^\circ(MF_nX_{m-n})$ is calculated from

$$\frac{n}{m}\Delta H_f^\circ(MF_m) + \left(\frac{m-n}{m}\right)\Delta H_f^\circ(MX_m)$$

with change in electronegativity. In contrast, the fluorinated silanes are actually stabilized with respect to the end members of the series.

Ternary compounds of Be and B are formed athermally, within the limits of experimental error, from the binary compounds. In fact, the facile redistribution reactions of boron halofluorides prevent separation of compounds from solution. Their equilibration can be followed by NMR spectroscopy (*153, 173*). The linear relations between enthalpies of boron halides in the same valence state and molecular weights contrast with nonlinear relations for aluminum halides (Fig. 6). Other metal chlorofluorides are stabilized and can be prepared by heating the component halides together. Oxygen substitution of Group VI and VII elements produces considerable geometric change and oxyfluorides which are more stable than expected. In general, the concept of bond additivity has only limited application in fluoride thermochemistry and there is no obvious second-order correction available apart from inverse power relations between bond length and bond strength (*38*).

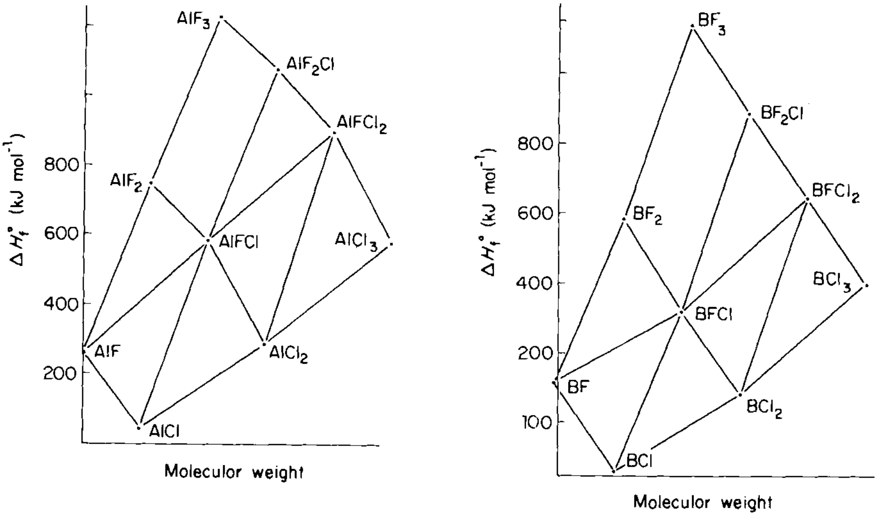


FIG. 6. Variation of enthalpies of boron and aluminum fluorides with chlorine substitution.

C. PERIODIC PATTERNS

Bond energy variations over the periodic table will be subject to perturbations which reflect the underlying atomic configurations. Compounds derived from main-group elements of Period 4, for example, will show discontinuities in properties from those of Period 3 because of the extra d-electron shell. Conversely, the insertion of an f-electron shell brings together the properties of the second and third transition series, especially in the earlier groups.

Plots of mean dissociation energies of fluorides against molecular weights illustrate these mainly nonlinear trends, the patterns of which can be used to predict missing heats of formation (Fig. 7).

Heats of formation and bond energies of Group VA to VIIIA gaseous fluorides are collected in Table XXII. From the first plot, for series with constant electron counts, it is possible to position IF_3 and deduce its heat of formation. This would be difficult to measure because, at well below room temperature, it breaks down to iodine and the pentafluoride. The spontaneous decomposition of ArF_2 under standard conditions is also predictable because the extrapolated dissociation energy is negative. From the second plot, for isoelectronic series with a constant electron/atom ratio, the positive dissociation energy predicted for KrF_6 should ensure molecular integrity if the large positive formation enthalpy can be overcome in its preparation.

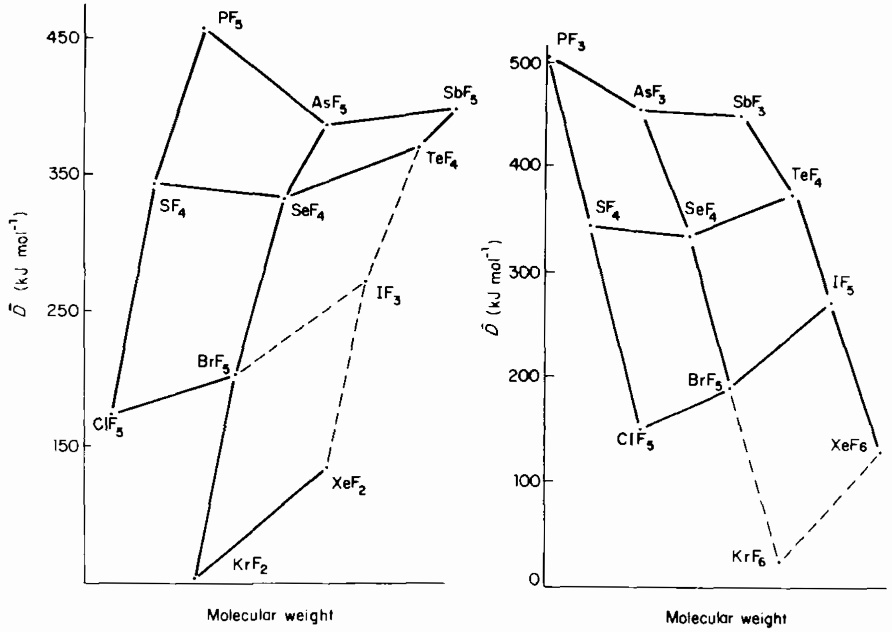


FIG. 7. Periodic patterns of isoelectronic fluoride dissociation energies.

The relative stability of two oxidation states of an element in even-electron fluorides along periods and groups is shown in Table XXIII. High ratios indicate enhanced stability of the lower state, instability of the upper state, or both. In oxygen chemistry, the strongly oxidizing properties of bromates, selenates, and arsenates compared with the Period 3 oxyanions are well known. (Comparison with Period 5 elements is difficult because of increase in coordination number in oxygen chemistry.) The only apparent anomaly is the high Cl ratio. This may reflect the considerable uncertainty in the enthalpy value for ClF_5, but it could be a genuine indication of its strong oxidizing properties. The low I ratio seems reasonable, although only an estimated enthalpy for IF_3 has been employed, because the reaction

$$5XF_3 \rightarrow X_2 + 3XF_5$$

is exothermic with X = I and endothermic with X = Br or Cl, in agreement with the known stabilities of halogen trifluorides.

Dasent estimated the heat of formation of the then unknown CrF_6 from a similar plot using Group IVB–VIB fluorides together with some main-group fluorides (*64*) which will obviously give a discontinuity. The effect of the "lanthanide contraction" diminishing from Groups

TABLE XXII

"ADDITIVITY" IN CHLORO-, OXO-, AND HYDROXOFLUORIDES

	$-\Delta H^\circ_{f(g)}$ (kJ mol^{-1})						
	Expt. (E)	Calc. (C)	(E) − (C)		Expt. (E)	Calc. (C)	(E) − (C)
$BeF_2{}^{a}$	796			$PbF_2{}^{b}$	664		
$BeFCl$	588	579	9	$PbFCl$	538	512	26
$BeCl_2$	362			$PbCl_2$	359		
$BF_3{}^{c}$	1135			$AlF_3{}^{d}$	1213		
BF_2Cl	888	891	−3	AlF_2Cl	1075	997	78
$BFCl_2$	641	647	−6	$AlFCl_2$	900	794	106
BCl_3	403			AlF_3	586		
$BF_3{}^{e}$	1135			$BF_2{}^{f}$	581		
BF_2OH	1099	1087	12	$BFCl$	320	332	−12
$BF(OH)_2$	1053	1040	13	BCl_2	83		
$B(OH)_3$	992			$SO_2F_2{}^{h}$	770		
$SF_4{}^{g}$	782			SO_2FCl	564	576	−12
SF_2O	548	540	8	SO_2Cl_2	382		
SO_2	297			$SF_6{}^{j}$	1221		
$MoF_6{}^{i}$	1559			SF_4O	—	946	—
MoF_4O	1255	1160	95	SF_2O_2	770	671	90
MoF_2O_2	1018	761	257	SO_3	396		
MoO_3	362			$WF_6{}^{k}$	1748		
$WF_6{}^{i}$	1722			WF_5Cl	1650	1552	98
WF_4O	1322	1246	76	WF_2Cl_2	1488	1355	133
WF_2O_2	915	769	146	WCl_6	570		
WO_3	293			$UF_6{}^{m}$	2187		
$ClF_5{}^{l}$	228			$UF_2O_2{}^{o}$	1651	1545	106
ClF_3O	152	132	20	UO_3	1224		
$ClFO_2$	35			$ReF_7{}^{n}$	1429		
				ReF_5O	1186	1178	8
				Re_2O_7	1101		

[a] From Farber and Srivastava (*85*).

[b] Solid values; from Cartwright and Woolf (*50*).

[c] From Higgins *et al.* (*114*), Porter *et al.* (*180*), and Srivastava and Farber (*215*).

[d] From Farber and Harris (*84*).

[e] From Porter *et al.* (*180*).

[f] From Srivastava and Farber (*215*)

[g] From Benson (*20*) and Vaughan and Muetterties (*228*).

[h] From Cartwright and Woolf (*49, 50*).

[i] From Atherton *et al.* (12).

[j] From Cartwright and Woolf (*49*).

[k] Liquid values; from Burgess *et al.* (43).

[l] From Barberi *et al.* (*13*).

[m] Solid values. Heat of sublimation of MoF_2O_2 assumed as 71 kJ mol^{-1}.

[n] From Burgess *et al.* (*40, 41*).

[o] From Cordfunke and Ouweltjes (*58*).

TABLE XXIII

COMPARISON OF DISSOCIATION ENERGIES OF FLUORIDES IN DIFFERENT OXIDATION STATES

$\bar{D}(M—F)_{MF_n}/\bar{D}(M—F)_{MF_{n+2}}$			
III/V	IV/VI	III/V	IV/VI
P[a]	S[b]	Cl[c]	
1.100	1.045	1.131	—
As[d]	Se[e]	Br[f]	—
1.174	1.106	1.076	
Sb[g]	Te[h]	I[i]	Xe[j]
1.120	1.090	1.008	1.040

[a] From Johnson *et al.* (*137*) and O'Hare and Hubbard (*170*).

[b] From Vaughan and Muetterties (*228*) and O'Hare *et al.* (*169*).

[c] From Evans *et al.* (*83*) and Bisbee *et al.* (33).

[d] From Woolf (*242*) and O'Hare and Hubbard (*167*).

[e] From Carré *et al.* (*48a*) and O'Hare *et al.* (*169*).

[f] From Stein (*218*).

[g] $\Delta H_f^\circ(SbF_{3(g)})$ includes an estimate of 83 kJ for the heat of sublimation.

[h] From Carré *et al.* (*48a*) and O'Hare *et al.* (*169*).

[i] $\Delta H_f^\circ(IF_{3(g)})$ obtained from Fig. 7 (*206*); all other values from direct experiment corrected using Table I.

[j] From Johnson *et al.* (*137*).

IVB–VIB is clearly shown in Fig. 8. (The heat of formation of CrF_6 cannot be deduced from the oxygen series, CrO_3, CrO_2F_2, $CrOF_4$, CrF_6, because it would deviate even further from linearity than the Mo and W analogs.)

Comment on heats of formation of fluoro-anions, and electron and fluoride-ion affinities of neutral fluorides, measured mass spectrophotometrically (*57, 185, 216, 222*) or derived from salt values obained by conventional calorimetry (*32, 45, 46, 105*) needs to be reserved until better agreement is reached between methods. However, from measurements on heats of formation of the predominantly ionic xenon fluoride adducts it has been possible to show the trend to increasing ionicity with pentafluoride partners Nb < Ta < Sb, which parallels the increasing Lewis acidity of these fluorides found by independent methods (*44*).

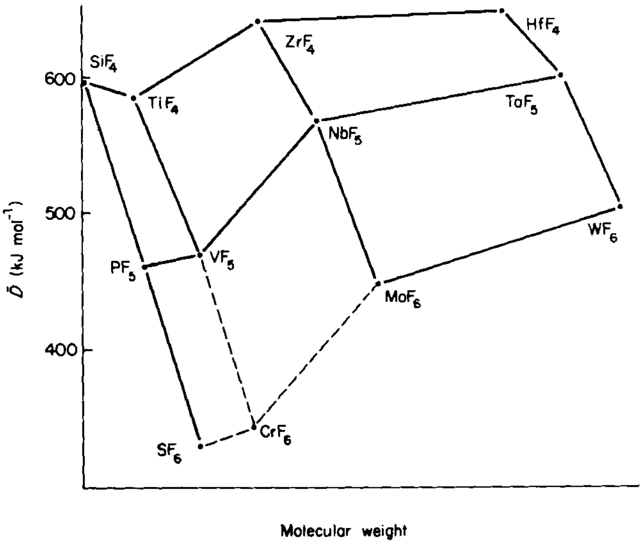


FIG. 8. Dissociation energies of Group IV, V, and VI highest fluorides.

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ADDENDUM

Additional references are given under the section headings.

I. A new book on combustion calorimetry (*25*) updates ref. (*214*).

III,A. Another fluorine bomb calorimeter is described (*18*) and further heats of formation of lanthanide trifluorides measured (*1, 11, 16*). A revised heat for UF_6 differs appreciably from previous values (*7*). Xenon difluoride has been used as a thermochemical oxidant (*19*).

III,F. More phase diagrams of complex fluorides have been explored using Knudsen cell mass spectrometry (*13, 15*), and electron impact studies have yielded enthalpies and bond energies (*1, 3*). The heat of formation of $MoF_{5(g)}$ has been confirmed (*12*). Solid state cells have been used with lanthanide trifluorides (*24*) and $NaNiF_3$ (*21*).

IV,A. Rittner's electrostatic model has been applied to the dissociation of metal halides (*5*) and Kapustinskii's equation to transition metal fluorides (*26*). A rough correlation between enthalpies of fluorides and the corresponding oxides and chlorides is suggested (*22*).

IV,C. Bond energies of cyanogen halides have been calculated (*8*).

IV,D. Dissociation energy–bond length relations have been proposed which take account of the atomic number of the atoms (*4*). The dissociation energies of Group VA monofluorides have been calculated using a Hulbert–Hirschfelder function (*23*) and thermodynamic functions calculated for di- and trifluorides (*2*). Another calculation of $D_0(F_2)$ has been made (*20*).

V,A. Further experimental work on dissociation energies in fluoride series underlines the warning given on the variability of high-temperature data. A new $\Delta H_f^\circ(BF_2)$ is 79 kJ different from the old value (*6*), and a maximum difference of 79 kJ appears in the dissociation energies of the sulfur fluorides (*9*). Values for tantalum (*17*) and platinum fluorides (*14*) are also now available.

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