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Fluoride Ion Affinities of GeF_4 and BF_3 from Thermodynamic and Structural Data for $(SF_3)_2GeF_6$, ClO_2GeF_5, and ClO_2BF_4

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$(SF_3)_2GeF_6$ is orthorhombic with $a = 6.142$ (1) Å, $b = 9.593$ (1) Å, $c = 7.458$ (1) Å, $V = 439.4$ (2) Å^3, and $\rho_{calcd} = 2.756$ g cm^{-3}. Full-matrix least-squares refinement using 299 independent observations (Mo K$\bar{\alpha}$, graphite monochromator) in space group *Pmnn* (No. 58) yielded weighted $R = 0.025$ (unweighted $R = 0.016$) from which SF_3^+ ions are seen to have $\sim C_{3v}$ symmetry with S–F = 1.515 (2), 1.519 (2) Å and F–S–F = 96.2 (1)°. Each SF_3^+ makes close contact with one F atom from each of three GeF_6^{2-} ions to give a distorted octahedron of F about S. The GeF_6^{2-} ions are almost octahedral with Ge–F = 1.783 (1), 1.787 (1) Å and cis F–Ge–F angles within 3σ of 90°, each F ligand being 2.37–2.42 Å from an S atom of an SF_3^+. Lattice energy calculation gives $\Delta H°(2SF_3^+(g) + GeF_6^{2-}(g) = (SF_3^+)_2GeF_6^{2-}(s)) = -383$ (12) kcal mol^{-1}. From dissociative pressure dependence on temperature, $\Delta H°((SF_3)_2GeF_6(s) = 2SF_4(g) + GeF_4(g)) = 42.9$ (6) kcal mol^{-1} and $\Delta S° = 125$ (2) cal mol^{-1} K^{-1}. Similarly, $\Delta H°(ClO_2GeF_5(s) = ClO_2F(g) + GeF_4(g)) = 29.1$ (4) kcal mol^{-1} and $\Delta S° = 90$ (1) cal mol^{-1} K^{-1}. Calculation of $\Delta H°(ClO_2^+(g) + GeF_5^-(g) = ClO_2^+GeF_5^-(s))$ gives -146 (5) kcal mol^{-1}. The derived enthalpy changes are $\Delta H°(GeF_4(g) + F^-(g) = GeF_5^-(g, \text{polymer})) = -100$ (6) kcal mol^{-1} and $\Delta H°(GeF_4(g) + 2F^-(g) = GeF_6^{2-}(g)) = -82$ (18) kcal mol^{-1}. ClO_2BF_4 is monoclinic with $a = 5.522$ (1) Å, $b = 8.646$ (1) Å, $c = 9.549$ (2) Å, $\beta = 98.01$ (1)°, $V = 451.4$ (2) Å^3, and $\rho_{calcd} = 2.269$ g cm^{-1}. The structure was refined in space group *Cc* (No. 9) to yield a weighted $R = 0.032$ (unweighted $R = 0.023$) from 577 independent reflections. All four fluorine atoms of the tetrahedral BF_4^- ion form van der Waals contacts with the chlorine atoms of neighboring ClO_2^+ ions. The closest of these contacts are nearly perpendicular to the plane defined by the centers of the chlorine and oxygen atoms. From measurements of the dissociation pressure of $ClO_2^+BF_4^-$ the previously reported value[1] of $\Delta H°(ClO_2F(g) + BF_3(g) = ClO_2BF_4(s)) = -24$ (1) kcal mol^{-1} has been confirmed. Lattice energy calculations have provided for evaluation of the following enthalpy changes: $\Delta H°(BF_3(g) + F^-(g) = BF_4^-(g)) = -92$ (6) kcal mol^{-1}; $\Delta H°(SF_4(g) = SF_3^+(g) + F^-(g)) = 211$ (8) kcal mol^{-1}; $\Delta H°(UF_6(g) + e^- = UF_6^-(g)) = -133$ (6) kcal mol^{-1}.

Introduction

The discovery[2] of what appears to be a thermodynamic threshold governing the intercalation of graphite by fluoro anions, MF_x^-, has required the evaluation of the thermodynamic stability of a number of such species. Since germanium tetrafluoride and fluorine are intercalated, in combination, by graphite[3] to form both GeF_5^- and GeF_6^{2-}, the first and second fluoride ion affinities of that molecule are each of interest. Evaluation of the fluoride ion affinity of boron trifluoride by Altshuller[4] yielded a value of -71 kcal mol^{-1}. This has been accepted by several authors[5,6] as the basis for other fluoride ion affinities and electron affinities. Sharpe,[7] however, has preferred a value of -91 kcal mol^{-1}, based upon the data of Bills and Cotton.[8] Although this latter value is in harmony with other fluoride ion affinities and electron affinities, its confirmation was clearly desirable to provide a firm basis for correction of affinities based upon the lower value. This paper describes the studies that have provided these fluoride ion affinities.

The salts $ClO_2^+GeF_5^-$ and $(SF_3^+)_2GeF_6^{2-}$, each of which dissociates to stable component species at easily accessible temperatures, have provided for the determination of the enthalpy changes

$$\Delta H°(ClO_2GeF_5(s) \rightarrow ClO_2F(g) + GeF_4(g)) \qquad (1)$$

$$\Delta H°((SF_3)_2GeF_6(s) \rightarrow 2SF_4(g) + GeF_4(g)) \qquad (2)$$

The salt $ClO_2^+BF_4^-$ also dissociates extensively at ordinary temperatures, and the enthalpy change

$$\Delta H°(ClO_2BF_4(s) \rightarrow ClO_2F(g) + BF_3(g)) \qquad (3)$$

has been reported[1] to be -24 ± 1 kcal mol^{-1}. This finding has been confirmed in the present study.

The crystal structures of the salts have been determined, ClO_2GeF_5 being reported in the accompanying paper[9] and the $(SF_3)_2GeF_6$ and ClO_2BF_4 structures in this paper. From that structural information, lattice energies for the latter two salts have been derived after the method of Bertaut[10] as modified by Templeton.[11] These provide enthalpy changes for the processes

$$\Delta H°(2SF_3^+(g) + GeF_6^{2-}(g) \rightarrow (SF_3)_2GeF_6(s)) \qquad (4)$$

$$\Delta H°(ClO_2^+(g) + BF_4^-(g) \rightarrow ClO_2BF_4(s)) \qquad (5)$$

The lattice enthalpy for ClO_2GeF_5

$$\Delta H°(ClO_2^+(g) + GeF_5^-(g) \rightarrow ClO_2GeF_5(s)) \qquad (6)$$

has been estimated from a simple linear empirical relationship between lattice energy and the reciprocal of the cube root of the formula unit volume.

The enthalpy change

$$\Delta H°(ClO_2F(g) \rightarrow ClO_2^+(g) + F^-(g)) \qquad (7)$$

is known from previously reported data;[12-14] hence, the values of

$$\Delta H°(GeF_4(g) + F^-(g) \rightarrow GeF_5^-(g)) \qquad (8)$$

$$\Delta H°(BF_3(g) + F^-(g) \rightarrow BF_4^-(g)) \qquad (9)$$

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(1) Christe, K. O.; Shack, C.; Pilopovich, D.; Sawodny, W. *Inorg. Chem.* **1969**, *8*, 2489.
(2) Bartlett, N.; McQuillan, B. W. In "Intercalation Chemistry"; Wittingham, S., Jacobson, A., Eds.; Academic Press: London, New York, 1982; Vol. I, pp 19–53.
(3) McCarron, E. M.; Grannec, Y. J.; Bartlett, N. *J. Chem. Soc., Chem. Commun.* **1980**, 890.
(4) Altshuller, A. P. *J. Am. Chem. Soc.* **1955**, *77*, 6187.
(5) Haartz, J. C.; McDaniel, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 8562.
(6) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 4992.
(7) Sharpe, A. G. In "Halogen Chemistry"; Gutman, V. Ed.; Academic Press: London, New York, 1967; Vol. I, p 1.
(8) Bills, J. L.; Cotton, F. A. *J. Phys. Chem.* **1960**, *64*, 1477.
(9) Mallouk, T. E.; Desbat, B.; Bartlett, N. *Inorg. Chem.*, preceding paper in this issue.
(10) Bertaut, E. F. *J. Phys. Radium* **1952**, *13*, 499.
(11) Templeton, D. H. *J. Che. Phys.* **1955**, *21*, 1629.
(12) Barberi, P. *Bull. Inf. Sci. Tech. Commun. Energ. At.* (*Fr.*) **1973**, *No. 180*, 55.
(13) Clyne, M. A. A. et al. *J. Chem. Soc. Faraday I* 1975, *71*, 322.
(14) Fisher, I. P. *Trans. Faraday Soc.* **1967**, *63*, 684.

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Table I. Crystal Data for $(SF_3)_2GeF_6$ and ClO_2BF_4

	$(SF_3)_2GeF_6$	ClO_2BF_4
cryst dimens, cm	0.022 × 0.018 × 0.020	0.04 × 0.02 × 0.02
space group	*Pmnn* (non-std setting of *Pnnm*, No. 58)	*Cc* (No. 9)
vol, $Å^3$	439.4 (2)	451.4 (3)
ρ_{calcd}, g cm^{-3}	2.756	2.269
cell dimens (*a*, *b*, *c* in Å; β in deg)	$a = 6.142$ (1), $b = 9.593$ (1), $c = 7.458$ (1)	$a = 5.522$ (1), $b = 8.646$ (1), $c = 9.549$ (2) Å; $\beta = 98.01$ (1)
radiation	Mo K$\bar{\alpha}$, graphite monochromator (λ 0.710 73 Å)	
2θ range, deg	3–45	
scan mode	θ–2θ	
scan rate	variable; max 50 s	
bkgd	$0.25\Delta\theta$ ($\Delta\theta = 0.50 + 0.347 \tan \theta$)	
hkl range	$\pm h, +k, +l$	$\pm h, +k, \pm l$
reflcns measd	687	684
orientation stds	$(\bar{4}11)$, $(\bar{1}61)$, (006); every 250 reflcns, no reorientation	$(\bar{3}1\bar{6})$, $(1\bar{5}\bar{4})$, $(\bar{1}1\bar{6})$; every 50 reflcns, frequent reorientation
intensity stds	$(\bar{4}11)$, $(\bar{1}61)$, (006); every 250 reflcns, no decay correction	$(11\bar{2})$, (060), $(\bar{1}3\bar{5})$; every 100 reflcns, nonlinear isotropic decay correction applied
abs coeff (μ_{calcd}), cm^{-1}	43.27	
transmission	47.4% min, 64.7% max	

are obtained directly from the complete thermodynamic cycles. In the case of the $(SF_3)_2GeF_6$ salt however, the enthalpy change

$$\Delta H°(SF_4(g) \rightarrow SF_3^+(g) + F^-(g)) \qquad (10)$$

was uncertain. This uncertainty derived from disagreement on the value of

$$\Delta H°(BF_3(g) + F^-(g) \rightarrow BF_4^-(g)) \qquad (9)$$

to be used to complete the cycle for the salt $SF_3^+BF_4^-(s)$. The crystal structure of this salt is accurately known[15] and the enthalpy change

$$\Delta H°(SF_3BF_4(s) \rightarrow SF_4(g) + BF_3(g)) \qquad (11)$$

has been evaluated in three independent studies.[16-18] Since the reported electron affinity[19] of UF_6 had been based on a questionable value for (9), an independent evaluation of

$$\Delta H°(UF_6(g) + e^- \rightarrow UF_6^-(g)) \qquad (12)$$

has been derived from the thermodynamic data available,[20] for the salt $NO^+UF_6^-(s)$. This also checks the lattice energy evaluations.

Experimental Section

Preparations and Structures. $(SF_3)_2GeF_6$. SF_4 and GeF_4 were brought together in a 2:1 molar ratio to produce a colorless solid $2SF_4 \cdot GeF_4$, which was purified by sublimation at room temperature. The apparatus, handling techniques, and starting material preparations are described in the accompanying paper.[9] Single crystals were grown by sublimation in quartz X-ray capillaries at 30–35 °C. Precession photographs indicated space group *Pnn*2 or *Pnnm*. A crystal mounted on a CAD-4 four-circle diffractometer provided a data set collected in the manner previously described.[9] Because of the ready dissociation of this compound, data were gathered at −97 ± 7 °C. They are given in Table I.

Table IIA. Positional Parameters for $(SF_3^+)_2GeF_6^{2-}$

atom	*x*	*y*	*z*
Ge	0.5000 (0)	0.5000 (0)	0.000 (0)
S	0.0000 (0)	0.25615 (8)	0.0651 (1)
F1	0.1842 (2)	0.1547 (1)	0.0267 (2)
F2	0.0000 (0)	0.1437 (2)	0.3475 (3)
F3	0.5000 (0)	0.1757 (2)	0.3819 (3)
F4	0.2946 (2)	0.4160 (1)	0.1298 (2)

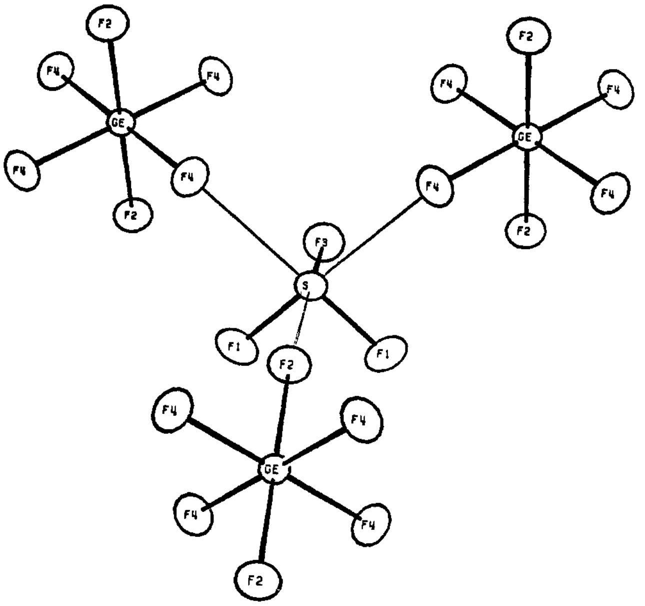

Figure 1. S coordination environment in $(SF_3^+)_2GeF_6^{2-}$.

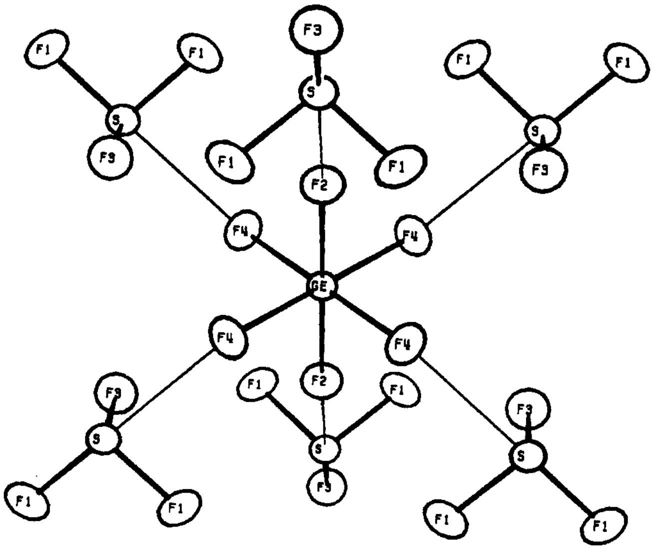

Figure 2. Ge coordination environment in $(SF_3^+)_2GeF_6^{2-}$.

The structure was successfully refined, as described elsewhere,[9] in the centric space group *Pmnn* (No. 58). Full-matrix least-squares refinement with anisotropic thermal parameters gave final convergence with weighted $R = 0.025$, unweighted $R = 0.016$, and esdouw = 1.463 for 42 variables and 299 independent observations. The largest parameter shift in the final refinement cycle was $<0.1\sigma$. A final difference Fourier gave no peaks with density greater than 0.141 e/$Å^3$. Positional and thermal parameters for $(SF_3)_2GeF_6$ are given respectively in Tables IIA and IIB (supplementary material). The structure factors are given in Table IIC (supplementary material).

The sulfur and germanium coordination environments in the $(SF_3)_2GeF_6$ structure are shown in Figures 1 and 2. While the space group requires C_s symmetry at S and C_{2v} symmetry at Ge, the SF_3^+ ion has essentially C_{3v} symmetry with all S–F bonds of equal lengths and all F–S–F angles equal within one standard deviation; the GeF_6^{2-} ion is almost a regular octahedron with all Ge–F bond lengths equal

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(15) Gibler, D. D.; Adams, C. J.; Fischer, M.; Zalkin, A.; Bartlett, N. *Inorg. Chem.* **1972**, *11*, 2325.

(16) Bartlett, N.; Robinson, P. L. *Chem. Ind. (London)* **1956**, 1351; *J. Chem. Soc.* **1961**, 3417.

(17) Steel, F.; Detmer, O. *Z. Anorg. Allg. Chem.* **1959**, *301*, 113.

(18) Cotton, F. A.; George, G. W. *J. Inorg. Nucl. Chem.* **1960**, *12*, 386.

(19) Beauchamp, J. L. *J. Chem. Phys.* **1976**, *64*, 929.

(20) Chatelet, J., private communication.

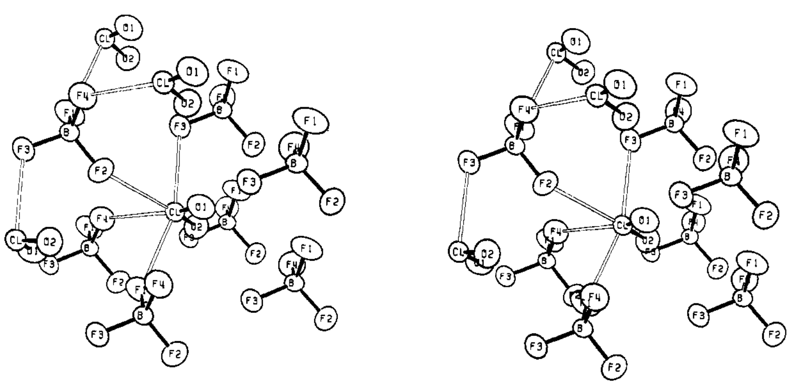

Figure 3. Stereoview showing coordination environment in ClO_2BF_4.

Table III. Bond Lengths (Å) and Angles (deg) for $(SF_3^+)_2GeF_6^{2-}$

Ge-F2	1.787 (1)	S-F2	2.367 (2)
Ge-F4	1.783 (1)	S-F3	1.515 (2)
S-F1	1.519 (1)	S-F4	2.420 (1)
Fe-Ge-F4	89.83 (5)	F2-S-F3	178.47 (8)
F1-S-F1	96.23 (10)	F2-S-F4	96.38 (4)
F1-S-F2	82.86 (6)	F3-S-F4	84.63 (5)
F1-S-F3	96.12 (8)	F4-S-F4	96.75 (6)
F1-S-F4	179.22 (7), 83.51 (5)		

Table IVA. Positional Parameters for $ClO_2^+BF_4^-$

atom	*x*	*y*	*z*
Cl	0.000	−0.7352 (6)	0.250
O1	−0.0377 (5)	0.0756 (2)	0.2990 (3)
O2	−0.0747 (4)	−0.1995 (2)	0.3237 (2)
B	0.4884 (6)	0.0675 (3)	0.0152 (4)
F1	0.6348 (4)	−0.0580 (2)	0.0578 (2)
F2	0.2652 (4)	0.0549 (2)	0.0626 (2)
F3	0.4492 (3)	0.0723 (2)	−0.1310 (2)
F4	0.6048 (3)	0.2003 (2)	0.0680 (2)

within 1σ and with F–Ge–F angles differing from 90° by about 3σ. Each sulfur atom makes close contacts with one F atom from each of three different anions, and so the cation–anion coordination in $(SF_3)_2GeF_6$ is 6:3, with each fluorine atom in the GeF_6^{2-} octahedron making a bridging contact (2.37–2.42 Å) to a sulfur atom. Fluorine atoms in the SF_3^+ ion make only van der Waals contacts (≥2.65 Å) with other fluorine atoms in the structure. The bridging by fluorine in this structure resembles that found[15] in SF_3BF_4, where the coordination is 3:3. The dimensions of SF_3^+ in $SF_3^+BF_4^-$ and $(SF_3^+)_2GeF_6^{2-}$ are not significantly different, and as has been remarked earlier,[15] the F–S–F bond angle has the same value as that of F–P–F in the isoelectronic relative PF_3. Bond lengths and angles for $(SF_3)_2GeF_6$ are given in Table III.

ClO_2BF_4. ClO_2F and BF_3 were combined in a 1:1 molar ratio. The pale yellow solid product was purified by sublimation and handled in a manner similar to that for $(SF_3)_2GeF_6$. Single crystals were grown in quartz capillaries at 25–30 °C. Precession photographs indicated space group *C*2/*c* or *Cc*. Data were gathered successfully at room temperature (Table I).

Refinement, in the acentric space group *Cc* (No. 9), with anisotropic thermal parameters, gave final convergence with weighted $R = 0.032$, unweighted $R = 0.023$, and esdouw = 1.828 for 72 variables and 577 independent observations. The largest parameter shift in the final refinement cycle was 0.1σ. The largest peak in the final difference Fourier was 0.274 e/Å^3. Positional and thermal parameters for ClO_2BF_4 are given respectively in Table IVA and IVB (supplementary material). The structure factors are given in Table IVC (supplementary material).

Upon examination of the data, it was found that three reflections gathered consecutively, the $\bar{2}2\bar{1}$, $\bar{2}20$, and $\bar{2}21$, showed the worst fit of F_o to F_c. Intensities of these reflections were apparently not fully counted to misorientation and were omitted from the final refinement.

A stereoview (Figure 3) shows the coordination about the Cl atom in ClO_2BF_4. Selected bond lengths and bond angles are given in Table V. The closest Cl···F contacts (F1 2.534 (2) and F3 2.580 (1) Å) are those approximately normal to the plane defined by the ClO_2^+. The other two Cl···F contacts (F2 2.704 (2) and F4 2.731 (2) Å) are in that plane. All four Cl···F contacts, together with the Cl–O bonds, complete a grossly distorted octahedral coordination about the Cl atom. The additional ligands perpendicular to the ClO_2 plane are placed similarly to those in the $ClO_2^+GeF_5^-$ structure,[9] where there are two crystallographically distinct ClO_2^+ ions. The in-plane Cl···F contacts in $ClO_2^+BF_4^-$ are different from each of the two arrangements in $ClO_2^+GeF_5^-$. Evidently the Cl···F contacts perpendicular to the ClO_2^+ plane are more significant than the others. The BF_4^- ions are almost tetrahedral.

Table V. Bond Lengths (Å) and Angles (deg) for $ClO_2^+BF_4^-$

Cl-O1	1.397 (2)	Cl-F4	2.731 (2)
Cl-O2	1.390 (2)	B-F1	1.380 (3)
Cl-F1	2.534 (2)	B-F2	1.376 (4)
Cl-F2	2.704 (2)	B-F3	1.383 (3)
Cl-F3	2.580 (1)	B-F4	1.377 (3)
O1-Cl-O2	119.0 (1)	F1-C-F4	78.18 (5)
O1-Cl-F1	93.0 (1)	F2-C-F3	73.34 (5)
O1-Cl-F2	87.9 (1)	F2-C-F4	71.97 (5)
O1-Cl-F3	91.6 (1)	F3-C-F4	90.40 (5)
O1-Cl-F4	158.2 (1)	F1-B-F2	110.8 (2)
O2-Cl-F1	98.4 (1)	F1-B-F3	108.9 (2)
O2-Cl-F2	152.01 (8)	F1-B-F4	108.9 (2)
O2-Cl-F3	96.62 (9)	F2-B-F3	108.3 (2)
O2-Cl-F4	82.25 (8)	F2-B-F4	109.9 (2)
F1-C-F2	87.07 (6)	F3-B-F4	110.1 (2)
F1-C-F3	159.69 (6)		

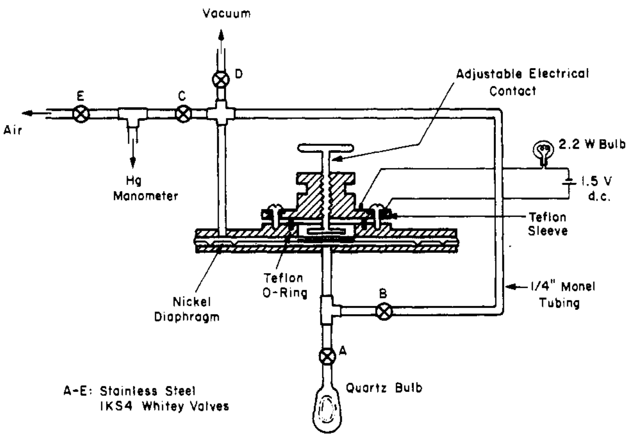

Figure 4. Apparatus for vapor pressure measurements.

Dissociation Pressure Measurements for $ClO_2^+GeF_5^-$ and $(SF_3^+)_2GeF_6^{2-}$. Vapor pressure measurements were made with use of a Monel diaphragm gauge as described by Cromer.[21] Each sample (1–2 g) was sublimed into a thin-walled quartz bulb partially collapsed to increase the surface area for good thermal contact. This was attached via Monel compression fittings to the gauge as shown in Figure 4.

The null point (no pressure difference across the nickel diaphragm) was established by closing valves A and C and opening valves B and D. For vapor pressure readings, the sample system and gauge were

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[21] Cromer, S. *U.S.A.E.C.* **1944**, *MDDC 803*.

Table VI. ln K_p vs. $1/T$ for $ClO_2^+GeF_5^-$ and $(SF_3^+)_2GeF_6^{2-}$

$10^3/T$, K^{-1}	$-\ln K_p$(obsd)	$-\ln K_p$(calcd)	$10^3/T$, K^{-1}	$-\ln K_p$(obsd)	$-\ln K_p$(calcd)
$ClO_2^+GeF_5$ ($\Delta H° = 29.1$ (4) kcal mol^{-1}; $\Delta S° = 90$ (1) cal mol^{-1} K^{-1}					
3.562	7.09	7.05	3.355	3.93	4.02
3.512	6.29	6.32	3.304	3.29	3.27
3.464	5.57	5.61	3.262	2.68	2.65
3.412	4.92	4.85			
$(SF_3^+)_2GeF_6^{2-}$ ($\Delta H° = 42.9$ (6) kcal mol^{-1}; $\Delta S° = 125$ (2) cal mol^{-1} K^{-1})					
3.661	15.97	16.01	3.473	11.98	11.96
3.593	14.62	14.55	3.416	10.60	10.73
3.529	13.19	13.17	3.288	8.02	7.97

fully immersed in a water bath. Valve B was closed, valves A and C were opened, and valves E and D were adjusted to find the null point at each bath temperature at equilibrium, the pressure being determined from a mercury column. The sample was pumped out briefly between pressure readings, which were reproducible within 1 or 2 torr at low temperature (0–10 °C) and within 4 or 5 torr at higher temperatures (25–35 °C). Log P vs. $1/T$ data for ClO_2GeF_5 and $(SF_3)_2GeF_6$ are given in Table VI. Since for ClO_2GeF_5 $K_p = [P_{Cl_2F}][P_{GeF_4}] = {}^1/_4P^2$ and for $(SF_3)_2GeF_6$ $K_p = [P_{SF_4}]^2[P_{GeF_4}] = 4P^3/27$, we have from the van't Hoff relation, $d(\ln K_p)/d(1/T) = -\Delta H°/R$

$$ClO_2GeF_5(s) = ClO_2F(g) + GeF_4(g)$$

$$\Delta H° = 29.1\ (4)\ \text{kcal mol}^{-1} \qquad \Delta S° = 90\ (1)\ \text{cal mol}^{-1}\ \text{K}^{-1}$$

$$(SF_3)_2GeF_6(s) = 2SF_4(g) + GeF_4(g)$$

$$\Delta H° = 42.9\ (6)\ \text{kcal mol}^{-1} \qquad \Delta S° = 125\ (2)\ \text{cal mol}^{-1}\ \text{K}^{-1}$$

The identifies of the gaseous species in equilibrium with the solids were established by infrared spectroscopy.

Lattice Energy Calculations

Electrostatic Terms. The electrostatic energy of a lattice of atoms of zero polarizability may be calculated exactly by the method of Bertaut,[10] provided the position and charge of each atom in the structure are known. This method involves the infinite sum in reciprocal space

$$U_{\text{elec}} = \frac{18\pi R^2}{V}\sum_{hkl}|F(hkl)|^2\frac{(\sin\alpha - \alpha\cos\alpha)^2}{\alpha^8} - \frac{3}{5R}\sum_j q_j^2$$

where $F(hkl) = \sum_j q_j \exp(2\pi i\mathbf{h}\cdot\mathbf{r}_j)$, $\alpha = 2\pi/d_{hkl}$, q_j is the charge on atom j, $\mathbf{h}\cdot\mathbf{r}_j = hx_j + ky_j + lz_j$, where (x_j, y_j, z_j) are the fractional coordinates of atom j, R is half the shortest interatomic distance in the crystal, d_{hkl} is the distance between lattice planes hkl, and V is the volume of the unit cell. In practice the sum must be terminated at some finite values of h, k, and l, and to estimate the error introduced thereby, the modification introduced by Templeton[11] has been used. In all calculations the termination of the series was chosen so as to ensure that this error was no greater than 0.2 kcal mol^{-1}. Fractional charges were assigned to atoms by using the electronegativity equalization procedure of Jolly and Perry.[22] Variation of these charges, within reasonable limits, produced small (1–3%) variations in the electrostatic part of the lattice energy; this is as expected since the multipolar interactions of complex ions in ionic crystals only amount to a few percent of the total lattice energy.[23]

London Energy Terms. The dipole-induced dipole dispersion energy (U_{dd}) is given by

$$U_{dd} = -{}^3/_2\sum_{i\neq j}\alpha_i\alpha_j\epsilon_i\epsilon_j r_{ij}^{-6}/(\epsilon_i + \epsilon_j)$$

where α and ϵ are respectively the polarizability and characteristic energy of the ion. The dipole-induced quadrupole energy (U_{dq}) is likewise given by a summation in r_{ij}^{-8}; it is however generally 10–15% of U_{dd}. We take U_{dq} to be 12% of U_{dd}.

The Closed-Shell Repulsion Term. A number of approaches to the calculation of closed-shell repulsion energies may be found in the literature. Ladd and Lee[24] have successfully used the expression

$$U_r = B\exp(-r_0/\rho)$$

where B is a constant eliminated by the criterion of energy minimization, r_0 the shortest interatomic distance, and ρ a parameter usually determined from compressibility data. In the absence of such data, Born and Mayer's equation[25] may be used:

$$U_r = b\sum_{i\neq j}(1 + q_i/n_i + q_j/n_j)\exp[(\bar{r}_i + \bar{r}_j - r_{ij})/\rho]$$

Here n is the number of electrons in the outer shell of the ion, q is the charge of the ion, $\bar{r}$ is its "basic radius", r_{ij} is the distance between ions i and j, and b and ρ are constants (10^{-12} erg molecule^{-1} and 0.32–0.36 Å, respectively). The range of variation of the parameter ρ is smaller when this expression for U_r is used. The Born–Mayer expression was used exclusively in the present calculations.

The Zero-Point Vibrational Energy and $\int C_p dT\ dT$ Terms. A complete lattice enthalpy at 298 K must include the enthalpy of cooling the gaseous ions to 0 K, the enthalpy of warming the crystal from 0 to 298 K, and the zero-point vibrational energy of the crystal.

For crystals containing relatively massive ions (SF_3^+, UF_6^-, GeF_6^{2-}, etc.), the zero-point energy (U_z) is small (0.2–0.4 kcal mol^{-1}). For crystals containing lighter ions, this term is more important and may be estimated from Waddington's correlation[26] of $S°_{298}$ with U_z. The specific heat (C_p) of the crystal is taken to be $3R$/ion; C_p is taken to be ${}^5/_2R$ for monatomic, ${}^7/_2R$ for diatomic, and $4R$ for nonlinear polyatomic ions in the gas phase.

Derivation of Parameters. The assignment of polarizabilities, characteristic energies, and basic radii to the atoms in a crystal is not straightforward. Although readily accepted values for these quantities for alkali and halide ions are available, serious errors (vide infra) can arise if the values of α, $\bar{r}$, and ϵ of fluoride ions are applied to fluorine atoms in a complex ion or molecule. The present approach has been, instead, to calculate the lattice energies of the molecular fluoride crystals UF_6 and SiF_4 (ignoring M–F interactions in the calculation of the repulsion energy, since the forces giving rise to it are of extremely short range). The sublimation enthalpies (and hence the lattice energies) are known for these compounds, and ϵ_F and $\bar{r}_F$ are derived parametrically, by using the energy minimization criterion, if values are assumed for α_F, α_M, and ϵ_M. The last two terms are of reduced parametric importance since M–F interactions account for only a small fraction of the dispersion energies of these compounds. The average of the values derived for ϵ_F, 46.90 (SiF_4) and 52.24 (UF_6) eV molecule^{-1}, and $\bar{r}_F$, 1.053 (SiF_4) and 1.079 (UF_6) Å, are used in subsequent calculations. These quantities are derived in the Appendix.

Calculations. The derived fluorine parameters were applied to calculations for the salts $SF_3^+BF_4^-$, $NO^+UF_6^-$, $(SF_3^+)_2GeF_6^{2-}$, $ClO_2^+BF_4^-$, and $K^+BF_4^-$. If the central atom in the anion is assumed to make no contribution to U_r, the lattice energy of the salt and the basic radius of the central atom in the cation may be calculated by minimizing the lattice energy with respect to variation in a crystallographic dimension r; r is chosen as the cube root of the unit cell volume, and so $dM/dr = 0$, where M is the Madelung constant. The following details for the salt $SF_3^+BF_4^-$ exemplify this approach:

From $(dU_L/dr)_{r=r_0} = 0$, we have

$$U_{\text{elec}} + 6U_{dd} + 8U_{dq} = b[\exp(2\bar{r}_S/\rho)\textstyle\sum_A + \exp((\bar{r}_S + \bar{r}_F)/\rho)\sum_B + \exp(2\bar{r}_F/\rho)\sum_C]$$

where $\sum_{A,B,C} = \sum_{i\neq j}(1 + q_i/n_i + q_j/n_j)r_{ij}/[\rho\exp(-r_{ij}/\rho)]$ and A refers to the sum over S–S, B over S–F, and C over F–F interactions. As pointed out by previous workers,[27] this equation is quadratic in

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(22) Jolly, W. L.; Perry, W. B. *Inorg. Chem.* **1974**, *13*, 2686.

(23) In these calculations we have taken the charge distributions of the individual atoms to be spherical. However, since the atoms are polarizable, they will in fact have multipolar charge distributions arising from the nonspherical arrangement of their (charged) near neighbors. The interactions of these multipoles will contribute another term to the electrostatic part of the lattice energy, which should be greater for NO^+, ClO_2^+, and SF_3^+ salts than for simple alkali halide salts. We have evaluated the largest of these, the dipole–monopole interaction term, for SF_3BF_4, by allowing each atom to become a permanent dipole (by virtue of its polarizability and the field created by the other point charges in the ion); the energy of this interaction is found to be ~0.1 kcal mol^{-1}. While this model is crude, it nevertheless provides an estimate of the order of magnitude of such interactions, which is indeed small.

(24) Ladd, M. F. C.; Lee, W. H. *Trans. Faraday Soc.* **1958**, *54*, 34.

(25) Born, M.; Mayer, J. E. *Z. Phys.* **1932**, *75*, 1.

(26) (a) Waddington, T. C. Ph.D. Thesis, Cambridge University, 1959. (b) Ladd, M. F. C.; Lee, W. H. *J. Inorg. Nucl. Chem.* **1960**, *14*, 14.

Table VII. Lattice Enthalpies and Basic Radii[a]

	SF_3BF_4	$NOUF_6$	ClO_2BF_4	KBF_4	$(SF_3)_2GeF_6$
U_{elec}, kcal	147.8	137.8	154.2	160.6	413.3
U_{dd}, kcal	37.14	26.21	35.13	22.37	72.73
U_{dq}, kcal	4.46	3.15	4.22	2.68	8.73
U_r, kcal	46.27	36.24	45.01	35.54	113.58
U_z, kcal	0.2	0.2	0.3	0.5	0.2
U_L(0 K), kcal	142.9	130.7	148.2	149.7	381.0
$\Delta H°_L$(298 K), kcal	144.1	131.6	149.4	149.9	382.8
$\bar{r}$, Å	$\bar{r}_S = 1.147$	$\bar{r}_{NO} = 1.262$	$\bar{r}_{Cl} = 1.150$	$\bar{r}_K = 1.193$	$\bar{r}_S = 1.170$

SF_3^+: $q_S = 0.9442+$, $q_F = 0.0186+$
BF_4^-: $q_B = 0.1420+$, $q_F = 0.2855-$
UF_6^-: $q_U = 0.5846+$, $q_F = 0.2641-$
ClO_2^+: $q_{Cl} = 1.083+$, $q_O = 0.0415-$
GeF_6^{2-}: $q_{Ge} = 0.3148+$, $q_F = 0.3858-$

	F	O	S	Cl	B	U	Ge	K	NO
α, Å^3	0.80	0.90	1.20	1.20	0.05	2.50	0.75	1.03	1.00
ε, eV	49.57	58.53	21.06	21.42	22.63	15.00	14.34	28.63	28.60

[a] For all calculations $\rho = 0.333$ Å and $\bar{r}_F = 1.066$ Å.

Table VIII. Data for the Determination of $\Delta H°_{298}(BF_3(g) + F^-(g) \rightarrow BF_4^-(g))$

	process	ΔH°, kcal mol^{-1}	ref
(a)	$^1/_2Cl_2(g) + {}^1/_2F_2(g) + O_2(g) \rightarrow ClO_2F(g)$	−8.0 ± 0.5	12
(b)	$ClO_2(g) \rightarrow {}^1/_2Cl_2(g) + O_2(g)$	−24.5 ± 0.8	13
(c) = (a) + (b)	$^1/_2F_2(g) + ClO_2(g) \rightarrow ClO_2F(g)$	−32.5 ± 1.0	
(d)	$F^-(g) \rightarrow {}^1/_2F_2(g) + e^-$	62 ± 1	38
(e) = (c) + (d)	$ClO_2(g) + F^-(g) \rightarrow ClO_2F + e^-$	29.5 ± 1.4	
(f)	$ClO_2^+(g) + e^- \rightarrow ClO_2(g)$	−246.6 ± 2.3	14
(g) = (e) + (f)	$ClO_2^+(g) + F^-(g) \rightarrow ClO_2F(g)$	−217 ± 3	
(h)	$ClO_2F(g) + BF_3(g) \rightarrow ClO_2BF_4(c)$	−24 ± 1	this work
(i) = (g) + (h)	$F^-(g) + ClO_2^+(g) + BF_3(g) \rightarrow ClO_2BF_4(c)$	−241 ± 3	
(k)	$ClO_2BF_4(c) \rightarrow ClO_2^+(g) + BF_4^-(g)$	149 ± 5	this work
(l) = (i) + (k)	$F^-(g) + BF_3(g) \rightarrow BF_4^-(g)$	−92 ± 6	

$\exp(\bar{r}_S/\rho)$, and so we obtain $\bar{r}_S$ and hence U_r from Born and Mayer's equation.

Calculation of the dispersion energy terms U_{dd} and U_{dq} requires that ε and α be assigned to the central atom of the cation (S in SF_3^+, Cl in ClO_2^+, NO^+, and K^+). The polarizability of cationic sulfur and chlorine atoms should be less than that of the neutral argon atom,[28] 1.6 Å^3, and slightly larger than that of K^+, for which a preferred value[29] of 1.029 Å^3 has been given. We take these to have a polarizability of 1.2 Å^3 and NO^+ (which occupies about the same volume as a K^+ ion in its salts) to have a polarizability of 1.0 Å^3. The characteristic energy is taken as nine-tenths of the second ionization potential of the free atom.

Table VII shows the calculated lattice enthalpies for $SF_3^+BF_4^-$, $NO^+UF_6^-$, $(SF_3^+)_2GeF_6^{2-}$, $ClO_2^+BF_4^-$, and $K^+BF_4^-$, and the derived basic radii for $S^{0.94+}$, $Cl^{1.1+}$, NO^+, and K^+. In these calculations a value of $\rho = 0.333$ Å was chosen, since this is the preferred value for the alkali fluorides.[27] Variation of ρ between 0.333 and 0.360 produced a variation of 1.5 kcal mol^{-1} in the lattice enthalpy calculated for $SF_3^+BF_4^-$. Likewise, a variation of $U_{dd} + U_{dq}$ by 25% (=9.5 kcal mol^{-1}) produced a change in the calculated lattice enthalpy of only 2.4 kcal mol^{-1}, becasue of a compensating change induced in U_r.

For $ClO_2^+GeF_5^-$ the method of calculation of the lattice enthalpy outlined above cannot be applied since the anion rearranges from a monomer in the gas phase to a cis-bridged polymer in the crystal. The lattice energy of this salt may be estimated from its formula-unit volume. Since the lattice energy of a simple A^+B^- salt is dominated by the Coulombic term (the repulsion energy and the dispersion energy terms being largely mutually canceling over a fairly wide range of formula-unit volumes), a roughly linear correlation between the lattice energy and $M/r_{A^+-B^-}$ is expected, where M is the Madelung constant and $r_{R^+-B^-}$ and $r_{R^+-B^-}$ is the shortest cation–anion distance in the crystal. Kapustinskii has shown,[30] however, that $M/r_{A^+-B^-}$ is relatively invariant with transformation from one structural type to another for the same ions A^+ and B^-; and so one should expect a linear correlation between the lattice energy and the inverse of the average primitive unit cell edge, i.e., the cube root of the formula-unit volume in the crystal. This linear correlation is shown in Figure 5. The correlation is particularly good among members of a given structural family, e.g., NaCl or CsCl. Where the dispersion energy term is expected to be large, because of highly polarizable or strongly coordinating ions (e.g., TlCl, ClO_2BF_4, and SF_3BF_4), a positive deviation is seen. The lattice enthalpy of $ClO_2^+GeF_5^-$ is therefore calculated simple from the U_L vs. $V^{-1/3}$ plot, allowing the same positive deviation as for $ClO_2^+BF_4^-$, to give $\Delta H°_L(ClO_2GeF_5) = 146 \pm 5$ kcal mol^{-1}.

Table IX. Thermodynamic Data for the Salt $NOUF_6$ and $\Delta H°_{298}(UF_6(g) + e^- \rightarrow UF_6^-(g))$

	process	ΔH°, kcal mol^{-1}	ref
(a)	$NO(g) + UF_6(g) \rightarrow NOUF_6(c)$	−52 ± 5[a]	20
(b)	$NOUF_6(c) \rightarrow NO^+(g) + UF_6^-(g)$	132 ± 5	this work
(c) = (a) + (b)	$NO(g) + UF_6(g) \rightarrow NO^+(g) + UF_6^-(g)$	80 ± 7	
(d)	$NO^+(g) + e^- \rightarrow NO(g)$	−213 ± 1	38
(e) = (c) + (d)	$UF_6(g) + e^- \rightarrow UF_6^-(g)$	−133 ± 7	

[a] The error estimate for this value is ours.

General Discussion and Conclusion

The dissociation energy determination and lattice energy calculation for $ClO_2^+BF_4^-(c)$, with other thermodynamic data given in Table VIII, provide the enthalpy change

$$\Delta H°(BF_3(g) + F^-(g) \rightarrow BF_4^-(g)) = -92 \pm 6 \text{ kcal mol}^{-1}$$

This is not significantly different from the value of −91 kcal mol^{-1} derived by Sharpe[7] from the data given[8] by Bills and Cotton. It indicates that the value of −71 kcal mol^{-1}, derived from Altshuller's measurements,[4] is seriously in error. Beauchamp,[19] in his ion cyclotron resonance study for the electron affinity of UF_6, used this latter value. With sub-

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(27) Jenkins, H. D. B.; Pratt, K. F. *Proc. R. Soc. London, Ser. A* **1977**, *356*, 115.
(28) Edgell, W. F. In "Argon, Helium, and the Rare Gases"; Cook, G. A., Ed.; Interscience: New York, 1961; Vol. I, p 151.
(29) Pirene, J.; Kartheuser, E. *Physica* **1964**, *30*, 2005.
(30) Kapustinskii, A. F. *Zh. Fiz. Khim.* **1934**, *5*, 59.

Table X. Thermodynamic Data for SF_3BF_4 and $(SF_3)_2GeF_6$, Including $\Delta H°$ for $SF_4(g) \rightarrow SF_3^+(g) + F^-(g)$, $GeF_4(g) + F^-(g) \rightarrow GeF_5^-$, and $GeF_4(g) + 2F^-(g) \rightarrow GeF_6^{2-}(g)$

	process	$\Delta H°$, kcal mol^{-1}	ref
(a)	$SF_4(g) + BF_3(g) \rightarrow SF_3BF_4(c)$	-25 ± 1	16-18
(b)	$SF_3BF_4(c) \rightarrow SF_3^+(g) + BF_4^-(g)$	144 ± 5	this work
(c) = (a) + (b)	$SF_4(g) + BF_3(g) \rightarrow SF_3^+(g) + BF_4^-(g)$	119 ± 5	
(d)	$BF_4^-(g) \rightarrow BF_3(g) + F^-(g)$	92 ± 6	Table IX
(e) = (d) + (c)	$SF_4(g) \rightarrow SF_3^+(g) + F^-(g)$	211 ± 8	
−2(e)	$2SF_3^+(g) + 2F^-(g) \rightarrow 2SF_4(g)$	-422 ± 16	
(f)	$2SF_4(g) + GeF_4(g) \rightarrow (SF_3)_2GeF_6(c)$	-43 ± 1	this work
(g) = (f) − 2(e)	$2SF_3^+(g) + 2F^-(g) + GeF_4(g) \rightarrow (SF_3)_2GeF_6(c)$	-465 ± 16	
(h)	$(SF_3)_2GeF_6 \rightarrow 2SF_3^+(g) + GeF_6^{2-}(g)$	383 ± 12	this work
(g) + (h)	$2F^-(g) + GeF_4(g) \rightarrow GeF_6^{2-}(g)$	-82 ± 18	
(a)	$ClO_2^+(g) + F^-(g) \rightarrow ClO_2F(g)$	-217 ± 3	Table IX
(b)	$ClO_2F(g) + GeF_4(g) \rightarrow ClO_2GeF_5(c)$	-29 ± 1	this work
(c) = (a) + (b)	$ClO_2^+(g) + F^-(g) + GeF_4(g) \rightarrow ClO_2GeF_5(c)$	-246 ± 3	
(d)	$ClO_2GeF_5(c) \rightarrow ClO_2^+(g) + GeF_5^-$(g, polymer)	146 ± 5	this work
(e) = (c) + (d)	$F^-(g) + GeF_4(g) \rightarrow GeF_5^-$(g, polymer)	-100 ± 8	

Table XI. Lattice Energy Calculations for SiF_4, UF_6, and OsO_4

	$\rho = 0.333$ Å			$\rho = 0.345$ Å		$\rho = 0.360$ Å	
	SiF_4	UF_6	OsO_4	SiF_4	UF_6	SiF_4	UF_6
$U_{dd} + U_{dq}$, kcal	16.62	29.37	27.64	17.84	31.59	19.60	34.69
U_z, kcal	0.5	0.2	0.5	0.5	0.2	0.5	0.2
U_r, kcal	11.40	19.91	18.63	12.62	22.13	14.38	25.23
ϵ_F, eV	46.90	52.24		51.00	56.53	56.98	63.32

	$\rho = 0.333$ Å			$\rho = 0.345$ Å		$\rho = 0.360$ Å	
	SiF_4	UF_6	OsO_4	SiF_4	UF_6	SiF_4	UF_6
ϵ_O, eV			58.53				
$\bar{r}_F$, Å	1.053	1.079		1.053	1.077	1.055	1.079
r_F, Å			1.144				

SiF_4: $q_F = 0.1710-$, $q_{Si} = 0.6840+$
UF_6: $q_F = 0.2210-$, $q_U = 1.3260+$ $\Big\}\ \alpha_F = 0.80$ Å^3

OsO_4: $q_O = 0.2915-$, $q_{Os} = 1.1660+$ $\}\ \alpha_O = 0.90$ Å^3

	Si	U	Os		Si	U	Os
α, Å^3	1.20	2.50	2.00	ϵ, eV	14.7	15.0	15.3

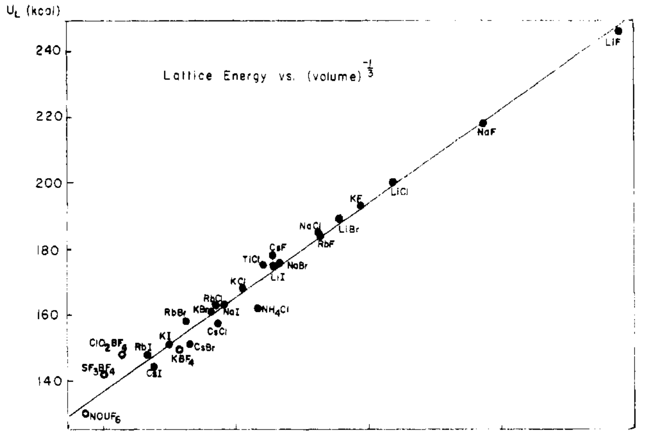

Figure 5. Lattice energies vs. (molecular volume)$^{-1/3}$: open circles, this work; shaded circles, ref 31.

stitution of −92 for −71 kcal mol^{-1} and with −62 kcal mol^{-1} for the heat of formation[38] of $F^-(g)$, Beauchamp's findings yield

$$\Delta H°(UF_6(g) + e^- \rightarrow UF_6^-(g)) = -135 \text{ kcal mol}^{-1}$$

This is gratifying close to the value of −133 kcal mol^{-1} (see Table IX) derived in this study using the salt $NOUF_6$. This agreement supports both the correctness of the value for the fluoride ion affinity of BF_3 and the lattice energy evaluations.

For the determination of the double fluoride ion affinity of GeF_4, using the readily dissociated salt $(SF_3)_2GeF_6$, the fluoride ion donor enthalpy of SF_4 had to be found. This was achieved via the salt SF_3BF_4, as revealed in Table X. This provides

$$\Delta H°(SF_4(g) \rightarrow SF_3^+(g) + F^-(g)) = 211 \pm 8 \text{ kcal mol}^{-1}$$

The derivation of the double fluoride ion affinity of GeF_4 is given in Table X. The relevant enthalpy change is

$$\Delta H°(GeF_4(g) + 2F^-(g) \rightarrow GeF_6^{2-}(g)) = -82 \pm 18 \text{ kcal mol}^{-1}$$

Chloryl fluoride, ClO_2F, is a poorer fluoro base than SF_4, its fluoride ion donor enthalpy being (see Table VIII)

$$\Delta H°(ClO_2F(g) \rightarrow ClO_2^+(g) + F^-(g)) = 217 \pm 3 \text{ kcal mol}^{-1}$$

This accounts for the stability of ClO_2GeF_5, which does not dismutate to yield $(ClO_2)_2GeF_6$, whereas SF_3GeF_5 was not preparable (in our hands) because of dismutation to $(SF_3)_2GeF_6$ and GeF_4. The salt ClO_2GeF_5, via the structural and thermodynamic evaluation set out in Table X, provided for the determination of the first fluoride ion affinity of GeF_4. The enthalpy change of interest is

$$\Delta H°(GeF_4(g) + F^-(g) \rightarrow GeF_5^-(\text{g, polymer})) = -100 \pm 6 \text{ kcal mol}^{-1}$$

If we take the enthalpy of polymerization of GeF_5^- to be comparable to that for SbF_5, which has been assessed[39] to be

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(31) Atoji, M.; Lipscomb, W. N. *Acta Crystallogr.* **1954**, *7*, 579.
(32) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 219.
(33) Patrode, W. I.; Papish, J. *J. Phys. Chem.* **1930**, *34*, 1494.
(34) Oliver, G. D.; Milton, H. T.; Grisard, J. W. *J. Am Chem. Soc.* **1953**, *75*, 2827.
(35) Mayer, J. E. *J. Chem. Phys.* **1933**, *1*, 270.
(36) Krebs, B.; Haase, K. *Acta Crystallogr., Sect B* **1976**, *B32*, 1334.
(37) Ogawa, E. *Bull. Chem. Soc. Jpn.* **1931**, *6*, 302.
(38) In all evaluations, $\Delta H_f°(F^-(g))$ has been taken to be −62 ± 1 kcal mol^{-1}. This is based on $\Delta H_f°(F(g))$ = 18.86 kcal mol^{-1} (from: "JANAF Tables"; Dow Chemical Co.: Midland, MI, 1977) and the electron affinity for F(g) of 81 ± 1 kcal mol^{-1} (recommended by: Sharpe, A. G. In "Halogen Chemistry"; Gutman, V.; Ed.; Academic Press: London, 1967; Vol. 1, pp 1-40).
(39) Fawcett, J.; Holloway, J. H.; Peacock, R. D.; Russell, D. K. *J. Fluorine Chem.* **1982**, *20*, 9-12.

-4 kcal mol^{-1}, then the first fluoride ion affinity of GeF_4 to form the monomer becomes

$$\Delta H^\circ(\mathrm{GeF_4(g)} + \mathrm{F^-(g)} \rightarrow \mathrm{GeF_5^-(g)}) = -96 \pm 6 \text{ kcal mol}^{-1}$$

Thus the first fluoride ion affinity of GeF_4 is 4–8 kcal more energetic than that of BF_3. The BF_4^- ion being one fluorine atom smaller than GeF_5^- has a packing volume 16 (±2) Å^3 less than the latter. Therefore, in small-cation structures, with close-packed ion arrangements, the lattice energy of fluoroborates can be ~5 kcal mol^{-1} more favorable than for related fluorogermanates. Thus for such salts the better fluoride ion acceptor ability of GeF_4 is largely offset by a poorer lattice energy. The lattice energy difference decreases, however, as the cation becomes larger. Then the fluorogermanate salts ought to be distinctly more stable than their fluoroborate relatives.

Recent observations[40] in these laboratories have determined that

$$\Delta H^\circ(\mathrm{PF_5(g)} + \mathrm{F^-(g)} \rightarrow \mathrm{PF_6^-(g)}) = -101 \pm 8 \text{ kcal mol}^{-1}$$

This is in accord with the comparable salt-forming abilities of GeF_4 and PF_5. The ClO_2^+ salts of GeF_{5n}^{n-} have comparable stabilities but neither fluoro acid forms a salt[41] (down to 0 °C) with IF_7. The salt $IF_6^+AsF_6^-$ however has negligible dissociation pressure at room temperature. This is because arsenic pentafluoride is a superior fluoride ion acceptor, for which we estimate

$$\Delta H^\circ(\mathrm{AsF_5(g)} + \mathrm{F^-(g)} \rightarrow \mathrm{AsF_6^-(g)}) = -111 \pm 4 \text{ kcal mol}^{-1}$$

The higher nuclear charge of the arsenic must be responsible for the higher fluoro acidity of AsF_5 relative to GeF_4. Similarly, the effective nuclear charge at the central atom in AsF_5 must be greater than in PF_5. This is a general situation for As(V) vs. P(V), compounds of the former being more powerful oxidizers than their phosphorus relatives.

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Appendix

For the compounds SiF_4 and UF_6 we have

$$U_r = b(1 + 2q_\mathrm{F}/n_\mathrm{F}) \exp(2\bar{r}_\mathrm{F}/\rho)\sum_{i\neq j}\exp(-r_{ij}/\rho)$$

$$U_\mathrm{dq} \simeq 0.12U_\mathrm{dd}$$

The lattice energy (U_L) is given by

$$U_\mathrm{L} = U_\mathrm{elec} + U_\mathrm{dd} + U_\mathrm{dq} - U_r - U_z$$

Since $(\mathrm{d}U_\mathrm{L}/\mathrm{d}r)_{r=r_0} = 0$, we have

$$U_\mathrm{elec} + 6U_\mathrm{dd} + 8U_\mathrm{dq} = b(1 + 2q_\mathrm{F}/n_\mathrm{F}) \exp(\bar{r}_\mathrm{F}/\rho)\sum_{i\neq j} r_{ij}/[\exp(-r_{ij}/\rho)]$$

Substituting $U_\mathrm{dq} = 0.12U_\mathrm{dd}$, we obtain

$$U_r = \left[\frac{U_\mathrm{L} + U_z - 0.8391U_\mathrm{elec}}{\sum_{i\neq j}(0.1609r_{ij}/\rho - 1)\exp(-r_{ij}/\rho)}\right]\sum_{i\neq j}\exp(-r_{ij}/\rho)$$

$$\bar{r}_\mathrm{F} = (\rho/2) \times \ln\left[\frac{U_\mathrm{L} + U_z - 0.8391U_\mathrm{elec}}{b(1 + 2q_\mathrm{F}/n_\mathrm{F})\sum_{i\neq j}(0.1609r_{ij}/\rho - 1)\exp(-r_{ij}/\rho)}\right]$$

We note that U_r (and thus $U_\mathrm{dd} + U_\mathrm{dq}$) is independent of the constant b and thus depends only on the choice of ρ, the calculated electrostatic energy, and the measured sublimation enthalpy. However, $\bar{r}_\mathrm{F}$ depends on both b and ρ.

The crystal structures of SiF_4 and UF_6 are accurately known,[31,32] and the polarizabilities, characteristic energies, and fractional charges assigned to each atom are shown in Table V. From these we obtain U_elec = 1.1 (1) kcal mol^{-1} for SiF_4 and 2.0 (1) kcal mol^{-1} for UF_6; the heats of sublimation are 6.2 kcal mol^{-1} (at 177 K) for SiF_4[33] and 11.8 kcal mol^{-1} (at 298 K) for UF_6.[34] The calculated values of ϵ_F and $\bar{r}_\mathrm{F}$ (from a polarizability of 0.80 Å^3 for F) are shown for three choices of ρ in Table VIII. Since the characteristic energy of an atom is related to its ionization potential, it is not surprising that the derived value of ϵ_F for these (nearly electroneutral) fluorine atoms is significantly higher than that calculated by Mayer[35] for the fluoride ion in the alkali fluorides. $\bar{r}_\mathrm{F}$ is likewise slightly smaller than the fluoride ion value determined by Jenkins and Pratt.[27] The agreement between the parameters derived from the SiF_4 and UF_6 calculations is reasonably good; when the lattice energy of SF_3BF_4 was calculated by using the two sets of parameters, the calculations differed by 1.3 kcal mol^{-1}. Average values of $\bar{r}_\mathrm{F}$ and ϵ_F are adopted for subsequent calculations. Oxygen parameters $\bar{r}_\mathrm{O}$ and ϵ_O are calculated from the OsO_4 structure[36] (for which the heat of sublimation[37] is 11.6 kcal at 300 K and U_elec = 2.5 (1) kcal mol^{-1}), assuming a polarizability of 0.90 Å$^+$ for the O atoms. Thus we obtain $\bar{r}_\mathrm{O}$ = 1.144 Å and <<e_O = 58.5 eV molecule^{-1}. The values of α and ϵ assigned to the central atom in the anion again have little impact on the result of the calculation.

Registry No. $(SF_3)_2GeF_6$, 91443-79-7; ClO_2GeF_5, 91199-69-8; ClO_2BF_4, 91443-81-1; SF_3^+, 25431-36-1; GeF_6^{2-}, 18588-21-1; BF_4^-, 14874-70-5; F^-, 16984-48-8.

Supplementary Material Available: Tables IIB and IIC (positional parameters and structure factors for $(SF_3^+)_2GeF_6^{2-}$) and IVB and IVC (positional parameters and structure factors for $ClO_2^+BF_4^-$) (11 pages). Ordering information is given on any current masthead page.

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(40) Rosenthal, G.; Bartlett, N., to be submitted for publication.

(41) Bartlett, N.; Yeh, S.; Kourtakis, K.; Mallouk, T. *J. Fluorine Chem.* **1984**, *26*, 97.