Thermochemistry of Hexafluoro-anions of M^{IV} (M = Si, Ti, Mn, or Re) and Lattice Energy Calculations for their Salts

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Enthalpies of solution of salts of MF_6^{2-} (M = Si^{IV}, Ti^{IV}, Mn^{IV}, or Re^{IV}), reactions of anions of this type for M = Os^{IV}, Ru^{IV}, and Re^{IV}, and enthalpies of hydrolysis of hexafluoro-manganate(IV) and -rhenate(IV) ions are reported. From these results and appropriate ancillary thermochemical data and extra-thermodynamic assumptions, we have estimated ion hydration enthalpies for a range of MF_6^{2-} ions, enthalpies of formation of $K_2[MnF_6]$, $Rb_2[MnF_6]$, $K_2[ReF_6]$, and several MF_6^{2-} ions, and two-fluoride ion affinities of the tetrafluorides of silicon, titanium, and manganese. The lattice enthalpies required in deriving these estimates have been obtained by an empirical and by a direct minimisation approach.

HEXAHALOGENOMETALLATE anions exhibit a wide range of reactivity with water, some showing considerable inertness, others hydrolysing ' instantly '. Calorimetric measurements on salts of inert anions will yield values for enthalpies of solution, whence ion hydration enthalpies for the anions may be obtained, *e.g.* $K_2[ReCl_6]$ (ref. 1) and $K_2[RuF_6]$.[2] Measurements on salts of anions which react rapidly with water will yield enthalpies of hydrolysis, whence, in favourable cases, electron affinities or halide-ion affinities may be estimated, *e.g.* $A[WF_6]$ (ref. 3) and $A_2[WBr_6]$ (A = alkali metal or alkaline-earth metal).[4] If the compound in question is stable and inert at pH 7, but hydrolyses readily in acidic or alkaline media, then both enthalpies of solution and of hydrolysis are obtainable, *e.g.* $K_2[ReCl_6]$ and related compounds.[4,5] Enthalpies of solution and of hydrolysis are directly obtained quantities, but ion hydration enthalpies, electron affinities, and similar thermodynamic parameters are indirectly obtained *via* the use of lattice enthalpies. The calculation of lattice energies for ternary salts ($A_x[MX_6]$) is more difficult than for binary ones, but considerable progress has been achieved.[6-8]

In this paper we report thermochemical investigations for salts of MF_6^{2-} anions where M = Si, Ti, Mn, or Re. Salts of these anions are not rapidly hydrolysed in water at pH 7, although enthalpies of solution of hexafluoromanganate(IV) ions need to be measured quickly to avoid significant hydrolysis. Salts of SiF_6^{2-} and of MnF_6^{2-} hydrolyse quickly in alkaline media to give products of known enthalpies. Hence enthalpies of formation of their salts can be obtained from measured enthalpies of alkaline hydrolysis. Salts of other MF_6^{2-} anions, *e.g.* where M = Re, Ru, or Os, react very slowly in solution; a catalyst is required. Metal-ion catalysis of solvolysis of chloro- and bromo-complexes,[9] *e.g.* hexabromometallates, is well established and has been examined kinetically for rhenium(IV) species.[10] ' Soft '[11] cations such as Hg^{2+} and Tl^{3+} are effective catalysts for chloro- and bromo-complexes, but ' hard ' cations will be needed for fluoro-complexes. Thorium(IV), zirconium(IV), aluminium(III), and beryllium(II) were found to catalyse solvolysis of benzyl fluoride,[11] and these and a range of other ' hard ' anions catalyse solvolysis of t-butyl fluoride.[12] The former cations also catalyse solvolysis of the hexafluoro-anions PF_6^- and AsF_6^-,[13] and of BF_4^-.[14] Thorium(IV) is known to catalyse aquation of the $[Co(NH_3)_5F]^{2+}$ cation.[9] We have found that of these only zirconium(IV) is an effective catalyst for aquation of the ReF_6^{2-}, RuF_6^{2-}, and OsF_6^{2-} anions; aluminium(III), lanthanide(III), and thorium(IV) cations are ineffective.

From experimental values for enthalpies of solution and enthalpies of hydrolysis under various conditions, and from two approaches to lattice enthalpy estimation for ternary salts, we obtain and report ion hydration enthalpies for a range of hexahalogenometallate anions and estimate fluoride-ion affinities for some tetrafluorides.

RESULTS

Enthalpies of Solution of $A_2[MF_6]$ *and* $A[MF_6]$.—The results of our direct calorimetric measurements of the enthalpies of solution of alkali metal and alkaline-earth salts $A_2[MF_6]$ and $A[MF_6]$ are reported in Table 1; all the salts used were anhydrous. The enthalpy of solution of these salts can sometimes be derived from the initial portion of the temperature-time record for (alkaline) hydrolysis. Thus an enthalpy of solution of *ca.* 60 kJ mol^{-1} estimated in this manner compares well with the previously reported[2] direct measurement for $K_2[ReF_6]$. For $Ba[MnF_6]$ an enthalpy of solution in water can only be obtained from such hydrolysis experiments; our estimate for this is 40 ± 2 kJ mol^{-1}. Our enthalpy of solution of $[NH_4]_2[SiF_6]$, 33.8 kJ mol^{-1} (Table 1), compares favourably with the value of 32.2 kJ mol^{-1} first reported for this salt,[15] but less well with values more recently quoted[16] of 27.8 kJ mol^{-1} (hexagonal form) and 26.6 kJ mol^{-1} (cubic form). The enthalpy of solution of $Rb_2[MnF_6]$ has been estimated as 94 kJ mol^{-1} from hydrolysis calorimetry experiments. It is possible to estimate enthalpies of solution of 45 kJ mol^{-1} for $Na_2[SiF_6]$, 70 kJ mol^{-1} for $K_2[SiF_6]$, and 76 kJ mol^{-1} for $K_2[TiF_6]$ from the (somewhat curved) plots of logarithms of solubility products against reciprocal temperature. Solution enthalpies increase markedly from sodium to caesium salts of the same anion, but stay similar for different salts of the same alkali metal.

TABLE 1

Solution enthalpies of MF_6^{2-} salts and of $K_2[ReCl_6]$ and $K_2[ReBr_6]$ at 298 K

Salt	Solution enthalpy [a]/ kJ mol^{-1}
$Na_2[SiF_6]$	30.8 ± 1.1(3)
$K_2[SiF_6]$	73.0 ± 2.0(4)
$Rb_2[SiF_6]$	86.1 ± 3.3(7)
$Cs_2[SiF_6]$	131.7 ± 0.9(5)
$[NH_4]_2[SiF_6]$	33.8 ± 0.9(3) [b]
$Ba[SiF_6]$	40.5 ± 0.3(3)
$K_2[TiF_6]$	74.0 ± 1.8(7)
$Cs_2[TiF_6]$	125.8 ± 2.8(3)
$K_2[MnF_6]$	61.1 ± 1.1(3)
$Rb_2[MnF_6]$	94 [c]
$Ba[MnF_6]$	40 [c]
$Na_2[ReF_6]$	32.9 ± 1.5(5)
$K_2[ReF_6]$	63.0 ± 0.3(4) [d]
$Cs_2[ReF_6]$	112.9 ± 0.2(3)
$Ba[ReF_6]$	35.4 ± 1.2(4)
$K_2[RuF_6]$	59.4 ± 1.5(5) [d]
$K_2[ReCl_6]$	43.50 ± 0.06 [e]
$K_2[ReBr_6]$	46.8 ± 0.4(4)

[a] Errors quoted represent 90% confidence limits (two-way analysis of variance, within and between samples and calibrations); the number of determinations is given in parentheses. [b] Previous values (kJ mol^{-1}) are 32.2,[15] 27.8 (hexagonal),[16] and 26.6 (cubic).[16] [c] From hydrolysis calorimetry experiments. [d] From ref. 2. [e] From ref. 1.

Hydrolysis of MF_6^{2-} *Salts*.—All the hexafluorometallates discussed so far in this paper hydrolyse slowly or not at all in neutral aqueous media. Salts of MnF_6^{2-} and SiF_6^{2-} hydrolyse rapidly in alkaline media, salts of ReF_6^{2-}, RuF_6^{2-}, and OsF_6^{2-} undergo hydrolysis extremely slowly or not at all in acid and in alkaline, as in neutral, solution. It is therefore necessary in these cases to use a catalyst to promote hydrolysis. We have carried out exploratory experiments on the ' hard ' [11] cations thorium(IV), zirconium(IV), hafnium(IV), aluminium(III), and some lanthanide(III) ions. Acid hydrolysis of MF_6^{2-} (M = Re, Ru, or Os) requires catalysis by zirconyl or hafnyl salts.[17]

Zirconium(IV)-catalysed aquation of MF_6^{2-} will be expected to produce the corresponding MCl_6^{2-} anions only at high chloride concentrations. The $OsCl_6^{2-}$ ion should be produced in 8 mol dm^{-3} hydrochloric acid; [18] even stronger hydrochloric acid may be needed to obtain the $ReCl_6^{2-}$ and $RuCl_6^{2-}$ anions.[19] We have confirmed the absence of $OsCl_6^{2-}$, $ReCl_6^{2-}$, and $RuCl_6^{2-}$ from reactions of the respective MF_6^{2-} anions with zirconium(IV) at hydrochloric acid concentrations less than 8 mol dm^{-3}, even after standing several days. However both u.v.–visible spectroscopy and calorimetric observations indicate that such reaction mixtures do undergo chemical change within minutes at room temperature. The u.v.–visible absorption changes sigmoidally with time, suggesting a two-stage reaction. The second stage follows first-order kinetics, once the initial reaction is virtually complete. The first reaction proved more difficult to characterise kinetically; often it makes only a very small contribution to the observed time-dependence of absorbance. However the results are not inconsistent with a first-order process.

A systematic variation of acid (0.05—1.0 mol dm^{-3}), chloride (0.05—1.0 mol dm^{-3}), and zirconium(IV) (0.01—0.05 mol dm^{-3}) concentrations for catalysed aquation of the OsF_6^{2-} anion {$[K_2(OsF_6)]$ = 1 g dm^{-3}} did not produce a readily interpretable pattern of observed first-order rate constants (the OsF_6^{2-} concentration was $\leqslant$0.05 mol dm^{-3}) corresponding to the second stage of reaction, nor of final spectra. Nonetheless it was noticeable that rates varied only little over the wide concentration ranges of H^+ and of Cl^- employed. The rate constants all lay between 1×10^{-4} and 5×10^{-4} s^{-1}, corresponding to half-lives of between 1 500 and 7 000 s; such long reaction times necessitate adiabatic calorimetry. The dependence of apparent rate constant on zirconium(IV) concentration was not simple, but was not inconsistent with the presence both of osmium(IV) and of zirconium(IV) in the transition state for this second stage.

The striking feature of the first stage of the reaction is that, at given concentrations of the other reagents, its half-life is independent of the nature of the hexafluoro-anion, being *ca.* 700 s in 0.01 mol dm^{-3} zirconium(IV) and 0.50 mol dm^{-3} hydrochloric acid, at 298.2 K. Moreover observation of the u.v. region of the spectrum for the reaction of ReF_6^{2-} with zirconium(IV) under these conditions showed a peak at 320 nm, not assignable to ReF_6^{2-}, whose height decreased according to first-order kinetics with a half-life again of *ca.* 700 s. We have recently observed analogous initial processes, again with half-lives of *ca.* 700 s, in zirconium(IV)-catalysed substitution at the PtF_6^{2-} and PF_6^- ions, by u.v.–visible and ^{31}P n.m.r. spectroscopy respectively. We feel that these observations imply that the first stage of the reaction involves the zirconium(IV) but not the MF_6^{2-} anion, and presume this reaction to be a depolymerisation process yielding a more active catalyst for fluoro-complex aquation. Kinetics of similar processes for lead(II) [20] and for titanium(III) [21] have been monitored at similar wavelengths, 270 nm and 340 nm respectively. Rates of depolymerisation of polynuclear lead(II) [20] and nickel(II) [22] species are fast, *e.g.* 690 s^{-1} at 298 K for $[Ni_4(OH)_4]^{4+}$; the rate of dedimerisation of titanium(III) is considerably slower, having a rate constant of *ca.* 2 s^{-1} at 298 K.[21] Rates of analogous processes for polynuclear cations of aluminium(III) and chromium(III) are slower again, while processes of this type may have half-lives of years for iron(III).[23] Our rate constant of *ca.* 1×10^{-3} s^{-1} for zirconium(IV) could well refer to depolymerisation of some polynuclear zirconium(IV) species; unfortunately there are no relevant kinetic data available.*

Enthalpies of Hydrolysis.—Hexafluoromanganate(IV) ions may be hydrolysed according to equations (1) to (3). Measured enthalpies of hydrolysis by these three methods are reported in Table 2, together with enthalpies of formation derived thence with the use of ancillary data from Table 3. The value for $\Delta H_f(K_2[MnF_6])$ obtained by the zirconium(IV)-iodide method is bracketed in Table 2 in view of the small uncertainty arising from the enthalpy contribution from zirconium(IV)–fluoride interaction; a

TABLE 2

Enthalpies of hydrolysis and of formation of potassium hexafluoromanganate

	Alkaline hydrolysis	Alkali + H_2O_2	Zr^{IV} + HCl + I^-
$\Delta H_{hyd.}$/kJ mol^{-1}	−230	−403	−104
ΔH_f/kJ mol^{-1}	−2 442	*	(−2 401) *

* See text.

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* Since this paper was written we have heard (D. H. Devia and A. G. Sykes, personal communication) that the rate-determining step in the depolymerisation of the tetranuclear zirconium(IV) species likely to be the major species in our stock solution has a half-life of *ca.* 600 s under conditions similar to those in our calorimetric measurements.

TABLE 3

Ancillary thermochemical data used in the derivation of enthalpies of formation and fluoride ion affinities

	$\Delta H_f^\ominus$/ kJ mol^{-1}	Ref.		$\Delta H_f^\ominus$/ kJ mol^{-1}	Ref.
$K^+(aq)$	−252.17	*a*	$H_2O(l)$	−285.830	*a*
$Mn^{2+}(aq)$	−220.75	*b*	$H_2O_2(l)$	−191.1	*b,i*
$F^-(aq)$	−335.35	*c*	$MnO_2(c)$	−502.3	*b*
$Cl^-(aq)$	−167.08	*a*	$MnF_4(c)$	−1 080	*f*
$I^-(aq)$	−56.90	*a*	$SiF_4(g)$	−1 615	*g*
$I_3^-(aq)$	−51.463	*d*	$TiF_4(c)$	−1 649	*h*
$OH^-(aq)$	−230.025	*a*	$K^+(g)$	514.6	*b*
$ReO_4^-(aq)$	−791.6	*e*	$Cs^+(g)$	459.8	*b*
$Cl_2(aq)$	25	*b*	$F^-(g)$	−270.7	*i*

[a] *J. Chem. Thermodyn.*, 1976, **8**, 603. [b] NBS Circular 500, 1952. [c] G. K. Johnson, P. N. Smith, and W. N. Hubbard, *J. Chem. Thermodyn.*, 1973, **5**, 793. [d] J. D. Cox, J. B. Pedley, A. Kirk, S. Seilman, and L. G. Heath, CATCH Tables, Halogen Compounds, University of Sussex, 1972. [e] R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609. [f] R. Hoppe, B. Müller, J. Burgess, R. D. Peacock, and R. Sherry, *J. Fluorine Chem.*, 1980, **16**, 189. [g] S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, 1963, **67**, 815. [h] E. Greenberg, J. L. Settle, and W. N. Hubbard, *J. Phys. Chem.*, 1962, **66**, 1345. [i] NBS Technical Note 270/3, 1968; a referee has pointed out that the most recent value for the electron affinity of fluorine (−328.0 kJ mol^{-1} at 298 K) leads to a value of −250.7 kJ mol^{-1} for$\Delta H_f^\ominus$ (F^-, g).

value of $\Delta H_f(K_2[MnF_6])$ of − 2 354 kJ mol^{-1} obtained *via* equation (2) suggests incomplete hydrolysis in alkaline peroxide.

$$K_2[MnF_6] + 4OH^- \longrightarrow 2K^+ + 6F^- + MnO_2 + 2H_2O \quad (1)$$

$$K_2[MnF_6] + H_2O_2 + 2OH^- \longrightarrow 2K^+ + 6F^- + Mn^{2+} + 2H_2O + O_2 \quad (2)$$

$$K_2[MnF_6] + 3I^- \longrightarrow 2K^+ + 6F^- + Mn^{2+} + I_3^- \quad (3)$$

From the enthalpy of hydrolysis of $K_2[ReF_6]$ in chlorine water, equation (4), which is -252 ± 5 kJ mol^{-1}, and

$$K_2[ReF_6] + 4H_2O + \tfrac{3}{2}Cl_2 \longrightarrow 2K^+ + ReO_4^- + 6F^- + 3Cl^- + 8H^+ \quad (4)$$

ancillary thermochemical data from Table **3** it is possible to estimate a value of −2 558 kJ mol^{-1} for $\Delta H_f(K_2[ReF_6],c)$.* The hydrolysis of $K_2[ReF_6]$ in zirconium(IV) oxochloride–hydrochloric acid media leads to precipitation of hydrated rhenium(IV) oxide. We have measured the enthalpy for this reaction as -25 ± 10 kJ mol^{-1}. However, due to considerable uncertainty as to the nature and composition of the precipitated $ReO_2(aq)$ and thus of its enthalpy of formation [we probably have a markedly different form of $ReO_2(aq)$ from the $ReO_2 \cdot 2H_2O$, of determined ΔH_f, of ref. 1], we cannot obtain a reliable value of $\Delta H_f(K_2[ReF_6])$ this way.

DISCUSSION

The lattice parameters used in our lattice-energy calculations are listed in Table 4. We have used two approaches to lattice-energy calculation, an empirical method based on electrostatic calculations incorporating assumptions about repulsion and van der Waals forces (and, in one case, Jolly and Parry's electronegativity equalisation principle [24]), and the direct minimisation method of Jenkins and Pratt.[6-8] The latter method is preferable in principle, but can only be used successfully when accurate crystal-structure information is available, preferably for more than one salt of a given anion.

Empirical Approach.—In our empirical approach to the estimation of lattice energies, the value of the repulsion energy for each salt $A_2[MF_6]$ was calculated from the simple Born–Mayer [25] expression $B\exp(-r/\rho)$ for the appropriate binary fluoride AF. Allowance was made for the increased number of A–F interactions, increased A–F distances, and the lower charge on the fluorines (*cf.* below) in the complex salts in comparison with the respective binary fluorides. The decrease in the charge on the fluorines is equivalent to an increase of 0.2—0.3 Å in the A–F distance. An analogous procedure was

TABLE 4

Lattice parameters for hexafluorometallate salts (lengths in Å)

Compound	Geometry	Dimensions	Ref.
$Na_2[SiF_6]$	Hexagonal	a = 8.859, c = 5.038	*a*
$K_2[SiF_6]$	Cubic	a = 8.133	*b*
$Rb_2[SiF_6]$	Cubic	a = 8.452	*c*
$Cs_2[SiF_6]$	Cubic	a = 8.919	*d*
$[NH_4]_2[SiF_6]$	Cubic	a = 8.395	*e*
$Ba[SiF_6]$	Rhombohedral	a = 4.76, α = 97·97°	*f*
$K_2[TiF_6]$	Hexagonal	a = 5.715, c = 4.656	*g*
$Cs_2[TiF_6]$	Hexagonal	a = 6.15, c = 4.96	*h*
$K_2[MnF_6]$	Hexagonal	a = 5.67, c = 9.35	*i*
$Rb_2[MnF_6]$	Cubic	a = 8.43	*i*
$Cs_2[MnF_6]$	Cubic	a = 8.92	*i*
$Ba[MnF_6]$	Rhombohedral	a = 4.86, α = 98.3°	*j*
$K_2[ReF_6]$	Hexagonal	a = 5.879, c = 4.611	*k*
$Cs_2[ReF_6]$	Hexagonal	a = 6.30, c = 4.99	*l*
$Ba[ReF_6]$	Rhombohedral	a = 4.92, α = 97.25°	*m*
$K_2[RuF_6]$	Hexagonal	a = 5.76, c = 4.64	*n*
$K_2[ReCl_6]$	Cubic	a = 9.840	*o*
$K_2[ReBr_6]$	Cubic	a = 10.385	*o*

[a] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Acta Crystallogr.*, 1964, **17**, 1408. [b] H. E. Swanson, N. T. Gilfrith, and G. M. Ugrinic, NBS Circular 539, 1955, vol. 5, p. 50. [c] H. E. Swanson, N. T. Gilfrith, and M. I. Cook, NBS Circular 539, 1956, vol. 6, p. 49. [d] See p. 19 of ref. *b*. [e] F. Hanic, *Chem. Zvesti*, 1966, **20**, 738; E. O. Schlemper and W. C. Hamilton, *J. Chem. Phys.*, 1966, **44**, 2499. [f] J. L. Hoard and W. B. Vincent, *J. Am. Chem. Soc.*, 1940, **62**, 3126. [g] S. Siegel, *Acta Crystallogr.*, 1952, **5**, 683. [h] B. Cox and A. G. Sharpe, *J. Chem. Soc.*, 1953, 1783. [i] H. Bode and W. Wendt, *Z. Anorg. Allg. Chem.*, 1952, **269**, 165; recent values obtained by R. Hoppe and B. Hofmann, *Z. Anorg. Allg. Chem.*, 1977, **436**, 65, are very similar. [j] R. Hoppe and K. Blinne, *Z. Anorg. Allg. Chem.*, 1957, **291**, 269. [k] G. R. Clark and D. R. Russell, *Acta Crystallogr.*, 1978, **31**, 894. [l] E. Weise, *Z. Anorg. Allg. Chem.*, 1956, **283**, 377. [m] R. D. Peacock, *J. Chem. Soc.*, 1956, 1291; D. Babel, *Struct. and Bonding (Berlin)*, 1967, **3**, 1. [n] R. D. Peacock, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 576. [o] H. D. Grundy and I. D. Brown, *Can. J. Chem.*, 1970, **48**, 1151.

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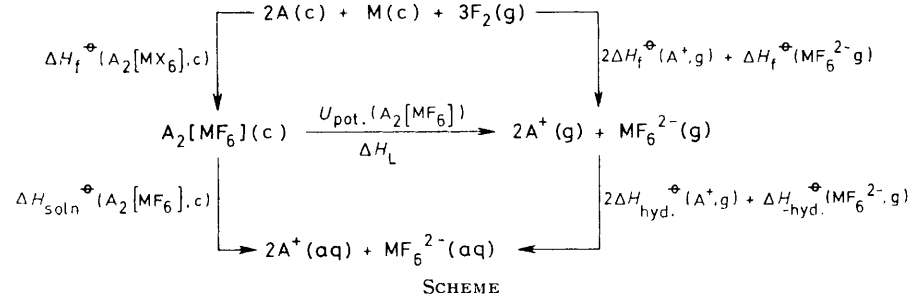
* It is not possible to obtain standard enthalpies of formation, $\Delta H_f^\ominus$, from our experimental results, but our enthalpies of formation, ΔH_f, under the conditions cited are unlikely to differ significantly from the respective $\Delta H_f^\ominus$ values.

employed for the barium salts Ba[MF$_6$]. The London energy ($U_{dd} + U_{qd}$) was calculated using the procedure outlined in ref. 26.

Direct Minimisation Method.—The alternative approach to the estimation of lattice enthalpies and subsequently derived thermodynamic parameters is the direct minimisation method, based on the Born–Fajans–Haber cycle, of Jenkins and Pratt.[6-8,27] For alkali-metal salts, the total lattice potential energy, $U_{pot.}(A_2[MX_6])$, is equal to the lattice enthalpy. For Ba[MF$_6$] salts an $RT/2$ term is added to $U_{pot.}$. Given good crystal-structure data the method can give an insight into the charge distributions in the complex MF_6^{2-} ions, especially where non-cubic crystals are concerned. The calculations are performed using the program LATEN [27] and the input parameters are the crystal-structure data, the ' basic ' radii of the cations [$\bar{r}_{Na^+} = 0.875$ Å, $\bar{r}_{K^+} = 1.189$ Å, $\bar{r}_{Rb^+} = 1.317$ Å, $\bar{r}_{Cs^+} = 1.472$ Å, $\bar{r}_{NH_4^+} = 1.265$ Å (point charge model for ion) and $\bar{r}_{Ba^{2+}} = 1.424$ Å], the polarisabilities, and characteristic energies of the ions concerned.



SCHEME

Charge Distributions in Complex Anions.—A central problem in estimating lattice energies for ternary salts is the establishment of the charge distribution within the complex ion. In some cases an estimate is available from techniques such as n.q.r. spectroscopy, in others one has to make reasonable assumptions. If the lattice parameters are available for several salts containing a given complex anion, then an optimum charge distribution can be obtained by intercomparison.

Ion Hydration Enthalpies.—The sums of the hydration energies of the constituent cations and anions of a salt can be calculated from the measured enthalpy of solution and the calculated lattice enthalpy (see the Scheme). A value of $-1\,101.6$ kJ mol^{-1} is given in several reference books for the hydration enthalpy of the proton. Halliwell and Nyburg's approach leads to the closely similar value of $-1\,091$ kJ mol^{-1}.[28] We shall use the former estimate here.

Hexafluorosilicate Anion.—Empirical approach. Once an appropriate assumption concerning the reference point for ion hydration enthalpies has been made, one can return to the problem of charge distribution within the anion. Figure 1 and Table 5 show how the hydration enthalpy of the SiF_6^{2-} anion depends on charge distribution for various salts. It will be seen that the various curves intersect within a relatively small area, which area would be smaller if the structural data for

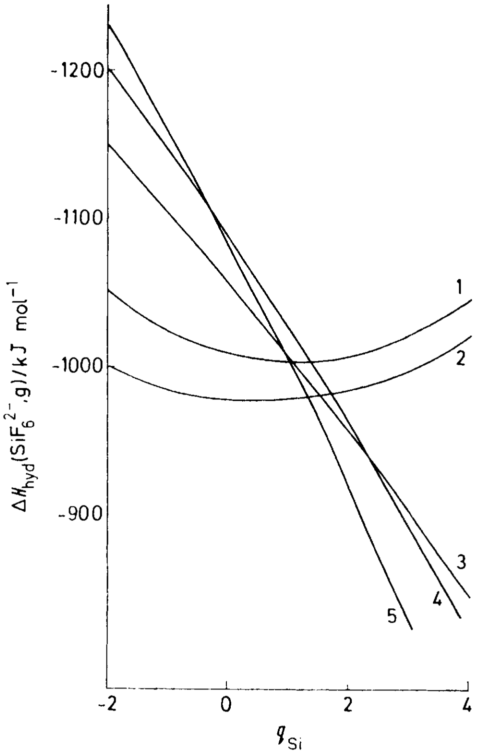


FIGURE 1 Dependence of estimated hydration enthalpy for the hexafluorosilicate(IV) anion on the effective charge on the silicon, q_{Si}, and on the nature of the cation; empirical method: (1) Na$^+$, (2) Ba^{2+}, (3) Cs$^+$, (4) Rb$^+$, (5) K$^+$

TABLE 5

Lattice enthalpies (ΔH_L) of $K_2[SiF_6]$ and derived ion hydration enthalpies ($\Delta H_{hyd.}$) for different charge distributions

q_{Si}	q_F	$U_{elec.}$ / kJ mol^{-1}	U_R / kJ mol^{-1}	ΔH_L * / kJ mol^{-1}	$\Delta H_{hyd.}(SiF_6^{2-})$ / kJ mol^{-1}
4.0	−1	−1 755	248	−1 455	−740
3.0	−0.833	−1 770	226	−1 547	−832
2.5	−0.75	−1 782	216	−1 591	−876
2.0	−0.667	−1 796	207	−1 634	−919
1.5	−0.583	−1 812	198	−1 675	−961
1.0	−0.5	−1 830	189	−1 716	−1 001
0.5	−0.417	−1 851	181	−1 756	−1 041
0	−0.333	−1 873	173	−1 794	−1 079
−0.5	−0.25	−1 899	165	−1 832	−1 117
−1.0	−0.167	−1 926	158	−1 868	−1 153
−1.5	−0.083	−1 956	151	−1 904	−1 189
−2.0	0	−1 988	144	−1 938	−1 223

* U_{London} ($= U_{dd} + U_{qd}$, *cf.* text) taken as -87 kJ mol^{-1}.

some of the salts * were better. The best estimate for the charge on the silicon, q_{Si}, appears to be *ca.* 1.8 ($q_F = -0.61$); we perforce assume the same charge distribution within the SiF_6^{2-} anion in each salt. This estimate corresponds to an ion hydration enthalpy of −1 000 kJ mol^{-1} (relative to −1 102 kJ mol^{-1} for the proton) for the SiF_6^{2-} anion. Fortunately this estimate only changes by a few kJ mol^{-1} for appreciable changes in the estimate for q_{Si} (*cf.* Figure 1).

From the measured enthalpy of solution of $[NH_4]_2[SiF_6]$ an apparent hydration enthalpy of −1 040 kJ mol^{-1} is obtained, taking $q_{Si} = 1.8$, for the SiF_6^{2-} anion. The difference of 40 kJ mol^{-1} can be attributed to the hydrogen-bonding contribution in solid $[NH_4]_2[SiF_6]$. This figure seems reasonable by comparison with estimates of *ca.* 80 kJ mol^{-1} for hydrogen bonding in solid ammonium fluoride.[29]

Direct minimisation approach. The enthalpy of hydration of the SiF_6^{2-} anion has previously been estimated by Jenkins and Pratt using their direct minimisation approach,[6,7] on the basis of 1 952 data [15] for the enthalpies of formation of the cubic salts $K_2[SiF_6]$, $Rb_2[SiF_6]$, $Cs_2[SiF_6]$, and $[NH_4]_2[SiF_6]$, to be −1 071 ± 75 kJ mol^{-1}. On the basis that some of the data used were considered unreliable (see section VIIID of ref. 6) they proposed the value −985 kJ mol^{-1} based on data for $[NH_4]_2[SiF_6]$. More recently,[7] incorporating some trigonal hexafluorosilicates ($Na_2[SiF_6]$ and $[NH_4]_2[SiF_6]$) they calculated a value of −965 kJ mol^{-1}. The provision of the solution enthalpy data of this present paper allows us to make a further estimate, making use of the Scheme above. From this cycle we obtain equations (5) and (6). We now use these equations and

$$\Delta H_{\text{hyd.}}^{\ominus}(SiF_6^{2-},g) = \Delta H_{\text{soln.}}^{\ominus}(A_2[SiF_6],c) - U_{\text{pot.}}(A_2[SiF_6]) - 2\Delta H_{\text{hyd.}}^{\ominus}(A^+,g) \quad (5)$$

$$\Delta H_{\text{hyd.}}^{\ominus}(SiF_6^{2-},g) = \Delta H_{\text{soln.}}^{\ominus}(Ba[SiF_6],c) - U_{\text{pot.}}(Ba[SiF_6]) - \Delta H_{\text{hyd.}}^{\ominus}(Ba^{2+},g) - \tfrac{1}{2}RT \quad (6)$$

the measured enthalpies of solution (Table 1), the calculated lattice energies, and the ancillary thermochemical data (based on the absolute hydration enthalpy of the proton of −1 101.6 kJ mol^{-1}): $\Delta H_{\text{hyd.}}^{\ominus}(Na^+,g) = -414.6$, $\Delta H_{\text{hyd.}}^{\ominus}(K^+,g) = -330.4$, $\Delta H_{\text{hyd.}}^{\ominus}(Rb^+,g) = -303.9$, $\Delta H_{\text{hyd.}}^{\ominus}(Cs^+,g) = -286.4$, $\Delta H_{\text{hyd.}}^{\ominus}(NH_4^+,g) = -331.4$, and $\Delta H_{\text{hyd.}}^{\ominus}(Ba^{2+},g) = -1\,360.5$ kJ mol^{-1}. Figure 2 shows the enthalpy of hydration, $\Delta H_{\text{hyd.}}^{\ominus}(SiF_6^{2-},g)$, plotted as a function of q_F the charge on the fluorine atoms in the separated fluorine atom model of the SiF_6^{2-} ion. The intersection points are widely spread but bearing in mind the significant uncertainties in the published crystal lattice parameters for $Na_2[SiF_6]$ (see above) and $Cs_2[SiF_6]$, and the fact that the data for $Ba[SiF_6]$ are nearly 40 years old and possibly subject also to some uncertainty, the results represent the best possible approach at the present time. The position of the line for $[NH_4]_2[SiF_6]$ will be appreciably affected by the significant hydrogen bonding in this substance (see above). On the basis of the results for the alkali-metal hexafluorosilicates alone we assign $\Delta H_{\text{hyd.}}^{\ominus}(SiF_6^{2-},g) = -971$ kJ mol^{-1} with $q_{Si} = 1.78$ and $q_F = -0.63$. These assignments may be compared with the recent estimate of q_F in this anion of −0.55 ($q_{Si} = 1.29$) from *ab initio* calculations.[30] Even closer values, of $q_F = -0.65$ and $q_{Si} = 1.9$, have recently been assigned by May.[31]

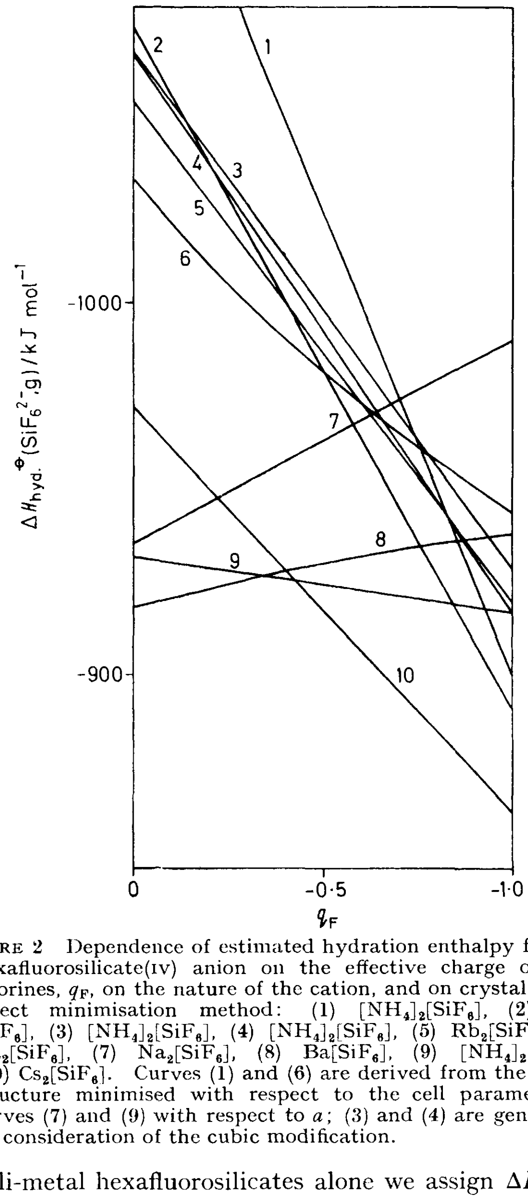


FIGURE 2 Dependence of estimated hydration enthalpy for the hexafluorosilicate(IV) anion on the effective charge on the fluorines, q_F, on the nature of the cation, and on crystal form; direct minimisation method: (1) $[NH_4]_2[SiF_6]$, (2) $K_2[SiF_6]$, (3) $[NH_4]_2[SiF_6]$, (4) $[NH_4]_2[SiF_6]$, (5) $Rb_2[SiF_6]$, (6) $Na_2[SiF_6]$, (7) $Na_2[SiF_6]$, (8) $Ba[SiF_6]$, (9) $[NH_4]_2[SiF_6]$, (10) $Cs_2[SiF_6]$. Curves (1) and (6) are derived from the *P*3*m*1 structure minimised with respect to the cell parameter *c*, curves (7) and (9) with respect to *a*; (3) and (4) are generated by consideration of the cubic modification.

Hexafluoromanganate Anion.—Empirical approach. Results are much less satisfactory with MnF_6^{2-} salts, mainly because atom positions have been derived from *X*-ray powder data and the uncertainties are considerable. There is also a degree of uncertainty in the enthalpies of solution of the caesium and barium salts due to their limited solubilities. A plot corresponding

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* Published data on the sodium salt are particularly suspect (R. Hoppe, personal communication).

to Figure 1 * gives q_{Mn} *ca.* 2, but the application of Jolly and Parry's electronegativity equalisation approach,[24] with the added assumption that the two negative charges on MnF_6^{2-} are distributed only over the fluorine atoms, gives q_{Mn} *ca.* 1.0. We choose $q_{\mathrm{Mn}} = 1.5$, whence a value of $-1\,000$ kJ mol^{-1} is obtained for the ion hydration enthalpy of MnF_6^{2-}; this value is relatively insensitive to changes in q_{Mn}.

Direct minimisation approach. Using our ΔH_{f} values for $K_2[MnF_6]$ and $Rb_2[MnF_6]$ from hydrolysis enthalpies (Table 6) in conjunction with the cycle (Scheme) we obtain equation (7). We can use our previous calculations of lattice-energy variation with q_{F} for Rb_2-

$$\Delta H_{\mathrm{f}}^{\ominus}(MnF_6^{2-},g) = U_{\mathrm{pot.}}(A_2[MnF_6]) - 2\,\Delta H_{\mathrm{f}}^{\ominus}(A^+,g) + \Delta H_{\mathrm{f}}^{\ominus}(A_2[MnF_6](c) \quad (7)$$

$[MnF_6]$ (Figure XV of ref. 7) and $K_2[MnF_6]$ (Figure XIV of ref. 7) and plot $\Delta H_{\mathrm{f}}^{\ominus}(MnF_6^{2-},g)$ against q_{F}.* Hence we assign $\Delta H_{\mathrm{f}}^{\ominus}(MnF_6^{2-},g) = -1\,823$ kJ mol^{-1} at a value of $q_{\mathrm{F}} = -0.93$ (*i.e.* $q_{\mathrm{Mn}} = 3.6$). These data can now be combined to give equation (8) and using our values for

$$\Delta H_{\mathrm{hyd.}}^{\ominus}(MnF_6^{2-},g) = \Delta H_{\mathrm{f}}^{\ominus}(K_2[MnF_6],c) - 2\Delta H_{\mathrm{f}}^{\ominus}(K^+,g) - \Delta H_{\mathrm{f}}^{\ominus}(MnF_6^{2-},g) - 2\Delta H_{\mathrm{hyd}}^{\ominus}(K^+,g) + \Delta H_{\mathrm{soln.}}^{\ominus}(K_2[MnF_6],c) \quad (8)$$

$\Delta H_{\mathrm{soln.}}^{\ominus}(K_2[MnF_6],c)$ from Table 1 we find $\Delta H_{\mathrm{hyd.}}^{\ominus}(MnF_6^{2-},g) = -912$ kJ mol^{-1}. This estimate differs somewhat from that derived using the empirical method (see above), but this is hardly surprising in the light of the difference between the two q_{Mn} values.

TABLE 6

Lattice enthalpies (kJ mol^{-1}) for $A_2[MF_6]$ and $A[MF_6]$ salts, calculated by the empirical method on the assumptions stated in the text, for $q_{\mathrm{M}} = 1.5$

$Na_2[SiF_6]$	$-1\,846$		
$K_2[SiF_6]$	$-1\,675$	$K_2[TiF_6]$	$-1\,649$
$K_2[MnF_6]$	$-1\,700$	$K_2[ReF_6]$	$-1\,653$ [a]
$Rb_2[SiF_6]$	$-1\,672$	$Rb_2[MnF_6]$	$-1\,674$
$Cs_2[SiF_6]$	$-1\,641$	$Cs_2[MnF_6]$	$-1\,627$
$[NH_4]_2[SiF_6]$	$-1\,680$ [b]		
$Ba[SiF_6]$	$-2\,323$		

[a] A lattice enthalpy of $-1\,680$ kJ mol^{-1} for $K_2[RuF_6]$ can be estimated from this value and the difference between the lattice enthalpies of $K_2[ReF_6]$ and $K_2[RuF_6]$ given in ref. 40. [b] Cubic form, calculated on the assumption that the cation is a 'hard sphere.'

Other Hexafluoro-anions.—Empirical approach. Insufficient data are available to estimate charge distributions in the other hexafluoro-anions; we shall use $q_{\mathrm{M}} = 1.5$ for them. Table 6 contains lattice enthalpies for the salts discussed in this paper, in each case calculated for $q_{\mathrm{M}} = 1.5$. Table 7 contains ion hydration enthalpies derived from these Table 6 lattice enthalpies. Table 7 also contains an estimate of the ion hydration enthalpy for the RuF_6^{2-} ion, calculated from the reported enthalpy of solution of $K_2[RuF_6]$ (ref. 2) and a lattice enthalpy for this salt calculated for $q_{\mathrm{Ru}} = 1.5$. The ion hydration enthalpies for the ReF_6^{2-} and RuF_6^{2-} anions in Table 7 obviously supersede our earlier estimates [2,†] based on more primitive (Born–Mayer) lattice enthalpy estimates. The anion hydration enthalpies in Table 7 show the expected variation with anion size; ionic radii for a range of 4+ cations are available in, for example, ref. 32.

TABLE 7

Single-ion hydration enthalpies (kJ mol^{-1}) for hexafluoro-elementate(IV) anions, derived *via* the empirical method (*cf.* text) for $q_{\mathrm{M}} = 1.5$; [a] values obtained by the direct minimisation method are given in parentheses

SiF_6^{2-}	$-1\,000$ [b]				
	(-971)				
TiF_6^{2-}	-940 [c]	MnF_6^{2-}	$-1\,000$		
	(-881)		(-912)		
		ReF_6^{2-}	-960	RuF_6^{2-}	-990
			(-903)		

[a] Values relative to $\Delta H_{\mathrm{hyd.}}(H^+) = 1\,102$ kJ mol^{-1} (ref. 28). [b] This value differs slightly from that given in Table 5, which refers to $K_2[SiF_6]$ only. [c] Estimated only from $K_2[TiF_6]$ as no lattice parameters are available for $Cs_2[TiF_6]$.

Direct minimisation approach. The paucity of crystal data on salts of other hexafluoro-anions limits the use of this approach. Using Siegel's structural data we find $U_{\mathrm{pot.}}(K_2[TiF_6]) = 1\,617$ kJ mol^{-1}, corresponding to $q_{\mathrm{Ti}} = 2.32$ ($q_{\mathrm{F}} = -0.72$). Using the measured $\Delta H_{\mathrm{soln.}}^{\ominus}(K_2[TiF_6]) = 74.0$ kJ mol^{-1} we estimate, using equation (9), that $\Delta H_{\mathrm{hyd.}}(TiF_6^{2-},g) = -881$ kJ mol^{-1}.

$$\Delta H_{\mathrm{hyd.}}^{\ominus}(TiF_6^{2-}) = \Delta H_{\mathrm{soln.}}^{\ominus}(K_2[TiF_6]) - U_{\mathrm{pot.}}(K_2[TiF_6]) - 2\Delta H_{\mathrm{hyd.}}(K^+,g) \quad (9)$$

The salt $K_2[ReF_6]$, whose enthalpy of formation is $-2\,559$ kJ mol^{-1} and enthalpy of solution 63.0 kJ mol^{-1}, has a lattice energy of 1 627 kJ mol^{-1} (see Figure XVIII of ref. 7), corresponding to $q_{\mathrm{Re}} = 1.36$ ($q_{\mathrm{F}} = -0.56$). These data indicate $\Delta H_{\mathrm{hyd.}}(ReF_6^{2-},g) = -903$ kJ mol^{-1}.

General.—The charge distributions in MF_6^{2-} which emerge from the lattice-energy calculations range from $q_{\mathrm{M}} = 1.36$ to 3.6 ($q_{\mathrm{F}} = -0.56$ to -0.93). This is an excessively wide range, with $q_{\mathrm{Mn}} = 3.6$ unacceptable, though little change in the data is required for a more plausible q_{Mn} to appear. A simple adaptation of Jolly and Parry's electronegativity equalisation approach from molecules to ions would suggest q_{M} *ca.* 1.0, but, as for the MnF_6^{2-} ion, we have chosen an arbitrary value of $q_{\mathrm{M}} = 1.5$ for most calculations involving MF_6^{2-} ions (see MnF_6^{2-} above). Fortunately the variation of hydration enthalpies with $q_{\mathrm{M}}(q_{\mathrm{F}})$ is gentle, so that if we assume a constant value of q_{M} in all anions, the anion hydration enthalpies estimated by the Jenkins and Pratt method will not change by more than *ca.* 30 kJ mol^{-1} from the values cited above. Estimates of ion hydration enthalpies derived from the two approaches are listed in Table 7. For comparative purposes we have calculated

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* Copies of these plots and of those for other hexafluoro-anions mentioned later in this paper may be obtained from the authors.

† There is, unfortunately, an error in our earlier paper; [2] the single-ion hydration enthalpy for ReF_6^{2-} should have read -936, not -999 kJ mol^{-1}.

TABLE 8

Anion hydration enthalpies for $ReCl_6^{2-}$ and $ReBr_6^{2-}$

	q_M	Lattice enthalpy/ kJ mol^{-1}	Ion hydration enthalpy/ kJ mol^{-1}
$K_2[ReCl_6]$	1.0	−1 501 [a]	−815
	1.36 [b]	−1 476 [a]	
	1.5	−1 458 [a]	−772
$K_2[ReBr_6]$	1.0	−1 445 [c]	−756
	1.5	−1 404 [c]	−715

[a] Including dispersion energy of −120 kJ mol^{-1}. [b] From n.q.r. estimate; M. Kubo and D. Nakamura, *Adv. Inorg. Chem. Radiochem.* 1966, **8**, 257. [c] Including dispersion energy of −129 kJ mol^{-1}.

lattice enthalpies of $K_2[ReCl_6]$ and $K_2[ReBr_6]$ for various charge distributions, and the corresponding ion hydration enthalpies of $K_2[ReCl_6]$ and $K_2[ReBr_6]$ (Table 8). These values supersede our earlier results.[5] The ion hydration enthalpies for the ReF_6^{2-}, $ReCl_6^{2-}$, and $ReBr_6^{2-}$ anions show the expected trend of decreasing magnitude with increasing anion size. They are more negative than the hydration enthalpies for the uninegative halide ions F^-, Cl^-, and Br^- (−490, −350, and −320 kJ mol^{-1} respectively [33]), but less negative than that for the smaller dinegative SO_4^{2-} anion [−1 100 kJ mol^{-1} (ref. 33)].

Enthalpies of Formation of MF_6^{2-} *Anions.*—These can be estimated by using the cycle shown in the top half of the Scheme. Enthalpies of formation (at 298.2 K) of $K_2[MnF_6]$ and of $K_2[ReF_6]$, −2 435 and −2 559 kJ mol^{-1}, have already been given (see above); the enthalpy of formation of $K_2[SiF_6]$ has been reported as −2 807 kJ mol^{-1} (ref. 15) and that of $K_2[TiF_6]$ estimated to be −2 909 kJ mol^{-1}.[34] From these data, the enthalpy of formation of K^+(g) (Table 3), and the respective lattice enthalpies, values of $\Delta H_f(MF_6^{2-},g)$ can be calculated. The results of such calculations, using lattice enthalpies determined by the empirical method described above (assuming $q_M = 1.5$) and, where possible, by the direct minimisation method, are given in Table 9. It is also possible to estimate $\Delta H_f(MnF_6^{2-},g)$ *via* the empirical lattice enthalpy for the rubidium salt; the value so obtained (−1 774 kJ mol^{-1}) is close to that obtained from the calculation on the potassium salt. However the value of $\Delta H_f(SiF_6^{2-},g)$ obtained from data on $Cs_2[SiF_6]$, −2 060 kJ mol^{-1}, using the empirically derived lattice enthalpy for $q_{Si} = 1.5$, is considerably smaller than that obtained by an analogous calculation from the potassium salt.

TABLE 9

Best estimates for enthalpies of formation (kJ mol^{-1}) of gaseous hexafluoroelementate(IV) anions at 298.2 K, derived [a] *via* the empirical method (*cf.* text) for q_M = 1.5; [b] values obtained by the direct minimisation method are given in square brackets

SiF_6^{2-}	−2 161	[−2 275 (ref. 6)] [−2 295 (ref. 7)]
TiF_6^{2-}	−2 289	[−2 321 (ref. 7)]
MnF_6^{2-}	−1 764	[−1 823]
ReF_6^{2-}	−1 935	[−1 961]
$ReCl_6^{2-}$	−863 [b]	
$ReBr_6^{2-}$	−622 [b]	

[a] From the potassium salts. [b] q_{Re} = 1.0 for the $ReCl_6^{2-}$ and $ReBr_6^{2-}$ anions.

For comparison we have included values of enthalpies of formation of the gaseous hexachloro- and hexabromorhenate(IV) anions in Table 9. These values have been obtained from the enthalpies of formation of the potassium salts reported earlier,[4] and lattice enthalpies of −1 501 and −1 445 kJ mol^{-1} respectively (*i.e.* for $q_{Re} = 1.0$). Changing the value of q_{Re} from this electronegativity-favoured value of 1.0 to the value of 1.5 used for all the hexafluoro-anions of the present study changes the $\Delta H_f(ReX_6^{2-},g)$ values by only *ca.* 40 kJ mol^{-1}, to $\Delta H_f(ReCl_6^{2-},g) = -906$ and $\Delta H_f(ReBr_6^{2-},g) = -663$ kJ mol^{-1} respectively.

Halide Ion Affinities.—Another interest in obtaining $\Delta H_f(MX_6^{2-})$ is in estimating electron affinities, and single and double halide ion affinities, given by equations (10), (11), and (12) respectively. This has been achieved

$$MX_6 + e^- \longrightarrow MX_6^- \quad \Delta H_E \qquad (10)$$

$$MX_5 + X^- \longrightarrow MX_6^- \quad \Delta H_X \qquad (11)$$

$$MX_4 + 2X^- \longrightarrow MX_6^{2-} \quad \Delta H_{2X} \qquad (12)$$

tolerably successfully for, *e.g.*, the electron affinity of tungsten hexafluoride and the fluoride ion affinity of tungsten pentafluoride,[3] and for the two-halide affinities of tetrachlorides and tetrabromides of tungsten and rhenium,[4] of selenium,[35] and of several other elements.[36]

The sparsity of thermochemical data on tetrafluorides restricts our estimates of two-fluoride ion affinities to those reported in Table 10. These values are derived from the $\Delta H_f(MF_6^{2-},g)$ values of Table 9, ancillary data from Table 3, and estimates of sublimation enthalpies of 98 and 142 kJ mol^{-1} for the tetrafluorides of titanium [37] and of manganese.[38] The assumptions and approximations involved in arriving at the Table 10 two-fluoride ion affinities mean that the uncertainties in these values are comparable to the differences between them. Comment will thus be restricted to the observation that all these affinities are favourable. More, and more accurate,* thermochemical data are required before our

TABLE 10

Two-fluoride ion affinities, ΔH_{2F} (see text), for tetrafluorides

	ΔH_{2F}/kJ mol^{-1}		
	MF_4(g)		MF_4(s)
Compound	Ref. 36	This work *	This work
SiF_4	−138	−5 (−119, −139)	
GeF_4	−242		
TiF_4	−228	−197 (−229)	−99
MnF_4		−285 (−343)	−143

* Values derived by the direct minimisation method are given in parentheses.

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* *Cf.* footnote *i* of Table 3; our Table 9 values use the value published in NBS Technical Note 270/3.

knowledge and understanding of two-fluoride ion affinities are as satisfactory as those for two-chloride and two-bromide ion affinities.[35]

EXPERIMENTAL

The salts $Na_2[SiF_6]$, $K_2[SiF_6]$, $[NH_4]_2[SiF_6]$, and zirconium(IV) oxochloride were obtained from B.D.H.; other reagents used in the calorimetric and kinetic studies were AnalaR grade.

The salts $Rb_2[SiF_6]$, $Cs_2[SiF_6]$, and $Ba[SiF_6]$ were prepared from H_2SiF_6 on carbonates or by ion exchange from the sodium salt; $K_2[TiF_6]$ and $Cs_2[TiF_6]$ from TiO_2 in HF and the alkali fluoride; $K_2[MnF_6]$ and $Rb_2[MnF_6]$ by Palmer's method;[39] $Ba[MnF_6]$ from $K_2[MnF_6]$ by metathesis; $K_2[ReF_6]$ and $K_2[RuF_6]$ as reported earlier;[40] $Na_2[ReF_6]$, $Cs_2[ReF_6]$, and $Ba[ReF_6]$ by ion exchange from the potassium salt; and $K_2[OsF_6]$ from $K[OsF_6]$.[41]

The kinetic runs were carried out in 10-mm silica cells in the thermostatted cell compartment of a Unicam SP800, SP1800, or SP8-100 recording spectrophotometer. Calorimetric experiments were conducted in an LKB calorimeter with ancillary apparatus as described earlier;[42] the LKB calorimeter's performance was monitored from time to time *via* determination of the enthalpy of solution of potassium chloride in water.[43] Samples of between 10 and 40 mg were used, with 30 or 100 cm^3 of water or aqueous hydrolysing medium, for the determinations of enthalpies of dissolution and of hydrolysis.

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