Thermochemistry of the Potassium Hexafluorometallates(III) of the Elements from Scandium to Gallium †

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The following standard enthalpies of formation at 25 °C have been determined by solution calorimetry: K_3ScF_6(c), −3 337; K_3TiF_6(c), −3 213; K_3VF_6(c), −3 026; K_3CrF_6(c), −2 977; K_3MnF_6(c), −2 849; K_3FeF_6(c), −2 807; K_3CoF_6(c), −2 634; K_3NiF_6(c), −2 558; K_3CuF_6(c), −2 407; K_3GaF_6(c), −3 001 kJ mol^{-1}. From these, the corresponding enthalpies of formation from gaseous K^+, M^{3+}, and F^- ions, *I*, have been calculated. When plotted against the number of 3*d* electrons on the metal ion, the values of |*I*| generate the familiar doubled-humped curve predicted by ligand-field theory, but the two humps are somewhat bigger than might have been expected.

The work described in this paper forms part of a series of studies of the relative stabilities of the di- and tri-positive oxidation states of the metals of the first transition series,[1-4] and was carried out some time ago [5] to test the validity of an assumption that was made in the first paper in the series [1] concerning the energies of high-spin tripositive species for elements beyond iron. This assumption was that the enthalpies of formation of such species from tripositive metal ions in the gas phase vary with the number of 3*d* electrons on the metal ion, *n*, in a similar way in the second half of the series (n = 5—10) as they do in the first (n = 0—5), and in a similar way to the corresponding quantities for dipositive species. This assumption has the support of ligand-field theory (provided that there is a similar arrangement of ligands around the metal atoms in all the species concerned, or that any differences have only a small effect on the energy), but it lacks experimental proof.

The potassium hexafluorometallates(III) were chosen for this study because they constitute an almost complete series of high-spin tripositive species.[6] The only missing member is the zinc compound, and the only one that seems not to be high spin at room temperature, the nickel compound, is by all accounts very close to being so.[7-9] Furthermore, all of them have basically the same structure, with octahedral coordination of the transition-metal atom.[10] The standard enthalpies of formation of these compounds have accordingly been determined, and from these, their standard enthalpies of formation from gaseous ions [equation (1)]. An outline of

$$3K^+(g) + M^{3+}(g) + 6F^-(g) \xrightarrow{I} K_3MF_6(c)$$

$$I = \Delta_fH^\circ[K_3MF_6(c)] - 3\Delta_fH^\circ[K^+(g)] - \Delta_fH^\circ[M^{3+}(g)] - 6\Delta_fH^\circ[F^-(g)] \quad (1)$$

the experimental work follows; further details may be found in ref. 5.

Experimental

Materials.—Hexafluorometallates(III). The scandium compound was made by heating $K_3[Sc(SO_4)_3]$ in fluorine. The titanate was made by dissolving titanium sponge in an excess of molten KHF_2 and leaching the product with formamide. The vanadate was prepared by heating $K_3[V(C_2O_4)_3]\cdot 3H_2O$ in hydrogen fluoride. The chromate was made by heating $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ in fluorine and reducing the product by heating it in nitrogen. The manganate was made by hydrofluorination of $K_3[Mn(CN)_6]$, the ferrate by direct fluorination of $K_3[Fe(CN)_6]$, and the cobaltate by direct fluorination of $K_3[Co(CN)_6]$.[7a] The nickelate was prepared by heating a fused mixture of KCl and $NiCl_2$ (3 : 1) in fluorine, reducing the product to nickel(II) by heating it in nitrogen, and then refluorinating it in very dilute fluorine ($F_2 : N_2$ = 1 : 15) at 210 °C for 20 h (*cf.* ref. 11). The copper compound was made by direct fluorination of $K_3[Cu(NO_2)_5]$, and the gallate was made similarly from $K_3[Ga(C_2O_4)_3]\cdot 3H_2O$. Attempts to make the zinc compound failed. Pure starting materials were used, and, except for the titanate, preparations were carried out in a tared nickel or platinum boat. The weights of the products were generally within 0.1% of the theoretical values for K_3MF_6, and in all cases within *ca.* 0.15%. (A difference of 0.15% in the weight corresponds to one of 0.2—1.0% in the weight change, depending on the starting material.) All air-sensitive materials were handled under dry nitrogen.

After suitable treatment, the hexafluorometallates(III) were analysed for potassium, metal, and fluorine by standard methods. Where possible, equivalent weights as oxidizing or reducing agents were also determined. In most cases, the results came within three parts per 1 000 of the theoretical values for K_3MF_6, and in all cases within seven parts.

The compounds were characterized by means of *X*-ray powder photography and i.r. spectroscopy. The powder photographs were all similar to each other, and to that of K_3AlF_6, prepared by direct fluorination of $K_3[Al(C_2O_4)_3]\cdot 3H_2O$. Except for the nickelate, there were no signs of any obvious impurities, and most of the lines could be accounted for on the basis of the unit cells given in Table 1. These have been expressed in a way that brings out their relationship to the unit cells of the cubic form adopted by compounds of this type at higher temperatures.[10] The existence of lines that could not be satisfactorily indexed was taken to reflect an incompleteness in the analysis. Other work has shown that the unit cells of these compounds may be of lower symmetry,[12] and of larger size,[12,13] than those reported here. Workers who have reported cubic unit cells at room temperature may either have missed the evidence of distortion [14] or obtained cubic forms of the compounds through quenching or impurity.[15]

The i.r. spectra were similar to those in the literature [16] and consistent with the presence of slightly distorted $M^{III}F_6$ octahedra; the distortions were enough to broaden the bands, or, in the case of K_3MnF_6, to split them. Only for the nickelate were there any signs of impurities.

As judged from the powder photograph, the impurities in the nickelate were K_2NiF_6, K_2NiF_4, and KF. The i.r. spectrum was consistent with this, in that it showed the presence of $Ni^{IV}F_6$ and $Ni^{II}F_6$. Rough intensity measurements, coupled with the overall stoicheiometry (K : Ni : F = 3 : 1 : 6), gave

† *Non-S.I. units employed*: B.M. ≈ 9.27 × 10^{-24} A m^2; cal = 4.184 J (for consistency with ref. 5).

Table 1. Cell parameters for the hexafluorometallates(III) at room temperature

Compound	a/Å	c/Å	Comments	Compound	a/Å	c/Å	Comments
K_3ScF_6	2 × 8.78	2 × 8.81	*a*	K_3FeF_6	2 × 8.61	2 × 8.72	*d, g*
K_3TiF_6	2 × 8.78	2 × 8.43	*b*	K_3CoF_6	2 × 8.54	2 × 8.62	*d, h*
K_3VF_6	2 × 8.72	2 × 8.34	*c*	K_3NiF_6	2 × 8.47	2 × 8.59	*i*
K_3CrF_6	2 × 8.58	2 × 8.65	*d, e*	K_3CuF_6	2 × 8.49	2 × 8.54	*j*
K_3MnF_6	2 × 8.74	2 × 8.27	*f*	K_3GaF_6	2 × 8.53	2 × 8.60	*d, k*

[a] H. Bode and E. Voss (*Z. Anorg. Allg. Chem.*, 1957, **290**, 1) reported a cubic unit cell with $a = 2 \times 8.73$ Å, but Peacock [6b] found it to be tetragonal. [b] Babel [10] reported $a = 8.56$, $c = 8.75$ Å, with $c/a > 1$. Compare, however, comment *c*. [c] J.-C. Cretenet (*Rev. Chim. Miner.*, 1973, **10**, 399) indexed the stronger lines in his photograph on the basis of the cell $a' = 6.04$, $c = 8.73$ Å, whence $a = 2^{\frac{1}{2}}a' = 8.54$ Å and $c/a > 1$. His *d* spacings are, however, very similar to ours. He attributes the remaining lines to lower symmetry. [d] These values are double those given in ref. 5 and account for most of the lines that could not be accounted for there. [e] Peacock [23] found $a = 8.56$, $c = 8.62$ Å. G. Garton and B. M. Wanklyn (*J. Cryst. Growth*, 1967, **1**, 49) give $a' = 12.08$, $c' = 12.16$ Å, corresponding to $a = 2^{\frac{1}{2}}a' = 2 \times 8.54$, $c = 2a'c'/(a'^2 + c'^2)^{\frac{1}{2}} = 2 \times 8.57$ Å. Pausewang and Rüdorff [12] obtained a powder photograph similar to that of K_3TiOF_5, and from the fact that crystals of the latter, although apparently tetragonal, are actually biaxial, they concluded that K_3CrF_6 too is probably only pseudo-tetragonal. They indexed the majority of the lines on the basis of the cell $a' = 6.05$ ($a = 2^{\frac{1}{2}}a' = 8.56$), $c = 8.59$ Å, and attributed the remainder to superstructure. A. de Kozak (*Rev. Chim. Miner.*, 1971, **8**, 301) concluded from rotation and Weissenberg photographs that the compound is 'quadratique, avec surstructure.' However, he did not determine its optical properties. For the sub-cell he gives $a' = 6.047$ ($a = 2^{\frac{1}{2}}a' = 8.552$) and $c = 8.620$ Å ($\pm ca.$ 0.1%). [f] Similar values were obtained by Peacock:[23] $a = 2 \times 8.75$, $c = 2 \times 8.30$ Å. [g] Peacock [23] found $a = 8.59$, $c = 8.66$ Å. Pausewang and Rüdorff [12] obtained similar results for K_3FeF_6 as they did for K_3CrF_6, and gave for the sub-cell $a' = 6.07$ ($a = 2^{\frac{1}{2}}a' = 8.58$), $c = 8.64$ Å. Precession photographs of poor quality suggest that *c* might be 3 × 8.7 Å (ref. 5). [h] Meyers and Cotton [14] have reported a cubic unit cell with $a = 8.55$ Å but say that distortions of up to 0.1 Å would probably have escaped their attention. Klemm *et al.*[7a] have also reported a cubic unit cell, with $a = 8.57$ Å. Compare, however, comment *i*. [i] Klemm *et al.*[7a] reported a cubic unit cell with $a = 8.50$ Å. However, H. Henkel and R. Hoppe (*Z. Anorg. Allg. Chem.*, 1969, **364**, 253) concluded that the compound is almost certainly tetragonal. They indexed a series of strong lines on their photograph on the basis of the cell $a = 8.46$, $c = 8.57$ Å. Some of the other lines corresponded to $KNiF_3$ and they concluded that some decomposition had taken place during the photography. Alter and Hoppe [7c] found that they were unable to prepare specimens that did not show signs of the presence of $KNiF_3$ in their powder photographs, and gave the constants as $a = 8.46$, $c = 8.56$ Å. Court and Dove [17] succeeded, however, in obtaining a sample that did not show evidence of the presence of other phases, and concluded that the compound is 'tetragonal or perhaps of lower symmetry.' [j] Klemm *et al.*[7a] quote the finding of E. Huss (Dissertation, Kiel, 1950) that the compound is cubic with $a = 8.50$ Å. Compare, however, comment *i*. [k] J. Chassaing (*Rev. Chim. Miner.*, 1968, **5**, 1115) has concluded that the room-temperature form (α) is a superstructure of the high-temperature form (γ) and deviates from cubic symmetry. His *d* spacings are similar to ours, only less complete. Alter and Hoppe,[13] however, have reported a cubic unit cell, with $a = 8.52$ Å from powder photography and $a = 5 \times 8.61$ Å from single-crystal work.

the approximate composition as $\frac{1}{3}K_3NiF_6 + \frac{1}{3}K_2NiF_6 + \frac{1}{3}(K_2NiF_4 + 2KF)$. The difficulty of obtaining K_3NiF_6 pure is well known.[7,11,17] Presumably, the free-energy change for the fluorination of $K_2NiF_4 + KF$ to $K_2NiF_6 + KF$ must be about the same per mole of F_2 as that for its fluorination to K_3NiF_6. If this is so, the difference between the enthalpy of formation of pure K_3NiF_6 and that of an impure sample of the same composition will be small [equation (2)]. Despite its high

$$\Delta(\Delta_f G^\ominus) \approx \Delta(\Delta_f H^\ominus) \approx 0 \qquad (2)$$

degree of impurity, our sample of the nickelate had a very similar magnetic moment (2.53 B.M. at room temperature) and reflectance spectrum to those reported in the literature.[7,8]

Other reagents. Scandium foil (99.9%), cobalt powder (99.99%), and K_2PtCl_4 were purchased from Johnson Matthey Ltd., titanium sponge (99.9%), iron powder (99.9%), and gallium rod (99.99%) from Koch-Light Ltd. The gallium was cast into thin flakes by melting it in a nitrogen-filled dry-box and spreading it over the surface of a watch-glass. Vanadium powder (99.6% V, 0.19% Mg, 0.11% O; under argon) was kindly given by Magnesium Elektron Ltd., and chromium powder (*ca.* 99.6% Cr, 0.34% Fe) by the Ministry of Aviation, from material being produced under contract to it at the B.S.A. Group Research Centre, Birmingham. Copper(II) oxide was prepared by dehydrating freshly precipitated copper(II) hydroxide under vacuum at 170 °C; analysis for copper indicated >99.7% CuO. Potassium hydrogendifluoride was prepared from AnalaR potassium carbonate and 40% hydrofluoric acid. Where appropriate, it was recrystallized from formamide to remove K_2SiF_6. Titration as an acid indicated ≥99.9% KHF_2. Stock solutions of 40% hydrofluoric acid (A: HF, $a H_2O$), dilute sulphuric acid (B: H_2SO_4, $b H_2O$), and hydrogen peroxide (C: H_2O_2, $c H_2O$) were made from AnalaR materials, and their composition determined by analysis ($a = 1.534$, $b = 52.78$, and $c = 43.46$). Potassium iodide was AnalaR. Air-sensitive materials were handled under dry nitrogen.

Calorimeter.—This consisted of a Dewar flask of about 350 cm^3 total capacity, fitted with a double lid [18] and a stirrer, and placed in a thermostat. Samples were held in a small metal drum with thin Polythene ends and released by means of a plunger. Temperatures were measured by means of a Beckmann thermometer, and temperature rises determined by Dickinson's method.[19] Calibration was by passing a steady electric current from an accumulator through a constantan heating coil for a measured period of time; the current was determined at intervals by measuring the potential difference across a standard resistance with a potentiometer, and the time was measured with a time interval meter (Allied Electronics Ltd., type 359B). To afford protection from the acids used, metal parts of the calorimeter in contact with the liquid were rhodium-plated, and other parts coated with paraffin wax. All heats were measured at *ca.* 25 °C.

The performance of the calorimeter was tested by measuring the heat of solution of tris(hydroxymethyl)methylamine (Eastman Kodak; dried, 99.9%) in 0.1001 mol dm^{-3} HCl and of magnesium (Koch-Light, 99.99%) in 1.000 mol dm^{-3} HCl. The results obtained agreed with the literature values [20,21] to within, on average, 0.2 kcal mol^{-1}.

Calorimetry.—Heats of solution were measured in 275 g of acid A or B. Reactions were carried out on a *ca.* 0.003 mol K_3MF_6 scale. To accelerate the dissolution of vanadium, iron, cobalt, and gallium, 0.20 cm^3 of a K_2PtCl_4 solution containing

10.0 mg cm^{-3} of platinum was added to the acid, and a correction of +0.42 cal made to the heat of solution.[22] In reactions involving an excess of potassium iodide, 10 g of the iodide were used. When two substances were dissolved simultaneously, they were separated in the sample holder with a Polythene disc.

Results are expressed in the form $\bar{X} \pm 2s$ [n], where n is the number of determinations, $\bar{X}$ is their mean, and s the standard deviation of the mean. Values based on a single determination are regarded as being provisional.

Scandate. Three heats of solution were measured: that of the scandate in A, that of scandium metal in A containing KHF_2, and that of KHF_2 in A. The results (kcal mol^{-1}) are given below (M = Sc).* The value for ΔH_2 includes a correction of

$$K_3MF_6(c) + [xHF, xaH_2O] \quad \Delta H_1 = -9.33 \pm 0.18 \text{ [3]}$$

$$M(c) + [3KHF_2, xHF, xaH_2O] \quad \Delta H_2 = -140.10 \text{ [1]}$$

$$3KHF_2(c) + [xHF, xaH_2O] \quad \Delta H_3 = 3(+0.79 \pm 0.04) \text{ [3]}$$

−0.27 kcal mol^{-1} for evaporation of HF and H_2O with the hydrogen evolved. The heat of formation of the scandate is given by equation (3).

$$\Delta_f H^\circ[K_3MF_6(c)] = 3\Delta_f H^\circ[KHF_2(c)] - \Delta H_1 + \Delta H_2 + \Delta H_3 \quad (3)$$

Titanate. The same procedure was used as for the scandate, except that the space above the liquid in the calorimeter was flushed with nitrogen before starting the measurements. The solutions at the end contained 99.5—99.7% of the original titanium as Ti^{III} after dissolution of the titanate, and 99.6—99.7% after dissolution of the metal. The results obtained were $\Delta H_1 = -13.72 \pm 0.23$ [3] and $\Delta H_2 = -114.95 \pm 0.47$ [3] kcal mol^{-1}. The latter includes a correction of −0.17 kcal mol^{-1} for the presence of 0.06% of oxygen in the titanium sponge.

Vanadate. The same procedure was used as for the titanate. The solutions at the end contained 99.8—100.1% of the original vanadium as V^{III} after dissolution of the vanadate, and 100.3—100.5% after dissolution of the metal. The results obtained were $\Delta H_1 = -7.59 \pm 0.12$ [3] and $\Delta H_2 = -64.06 \pm 0.33$ [3] kcal mol^{-1}. The latter includes a correction of −0.09 kcal mol^{-1} for the presence of magnesium and oxygen in the vanadium.

Chromate. The same scheme was used as for the scandate. The solutions at the end had no reducing power. The results obtained were $\Delta H_1 = -9.00 \pm 0.16$ [3] and $\Delta H_2 = -53.76$ [1] kcal mol^{-1}. The latter includes a correction of −0.12 kcal mol^{-1} for the presence of iron in the chromium.

Manganate. A provisional value for the heat of formation was obtained by comparing the heat of solution of the compound in B containing an excess of potassium iodide with that of the cobaltate. The sample used was one that had been prepared by Peacock's method,[23] and found to have very similar properties to material prepared in the way described above. In tests, it had liberated 99.6—99.8% of the theoretical amount of iodine from acid KI. The result obtained was $\Delta H = -5.58$ [1] kcal mol^{-1}, compared with −18.05 kcal mol^{-1} for K_3CoF_6. The heat of formation was calculated from equation (4).

$$\Delta\{\Delta_f H^\circ[K_3MF_6(c)]\} \approx \Delta\{\Delta_f H^\circ[M^{2+}(aq)]\} - \Delta(\Delta H) \quad (4)$$

Ferrate. Three heats of solution were measured: (a) that of the ferrate in A to which some water had been added, (b) that of iron powder in A containing KHF_2, and (c) that of hydrogen peroxide solution C in the solution obtained from (b). The calorimeter was flushed with nitrogen before carrying out reaction (b), and was flushed again at the end of (b) before carrying out reaction (c). Slightly less hydrogen peroxide was used than that required to convert all the Fe^{II} into Fe^{III} so that any loss of Fe^{II} by aerial oxidation could be determined by titration with $K_2Cr_2O_7$ at the end. From test runs without hydrogen peroxide, a loss of about 1.5% was expected, and in two of the calorimetric runs, such a loss was found. In a third run, the loss appeared to be significantly less than 1.5%, and this was attributed to decomposition of some of the hydrogen peroxide. The results (kcal mol^{-1}) obtained were as follows. The value for ΔH_b includes a correction of

$$K_3FeF_6(c) + [xHF, (xa + \tfrac{1}{2}c + 1)H_2O] \quad \Delta H_a = -7.65 \pm 0.26 \text{ [3]}$$

$$Fe(c) + [3KHF_2, xHF, xaH_2O] \quad \Delta H_b = -25.03 \pm 0.34 \text{ [2]}$$

$$\tfrac{1}{2}[H_2O_2, cH_2O] + [3KHF_2, Fe(HF_2)_2, (x-4)HF, xaH_2O] \quad \Delta H_c = -43.63 \pm 0.20 \text{ [2]}$$

−0.18 kcal mol^{-1} for evaporation of HF and H_2O with the hydrogen evolved, and of $\xi\Delta H'$ for aerial oxidation of Fe^{II} to Fe^{III}, where ξ is the fraction oxidized and $\Delta H'$ is the heat of oxidation. The latter was estimated to be −21.0 kcal mol^{-1} from the relation (5) where ΔH_d (see below)

$$\Delta H' \approx \Delta H_c - \Delta H_d - \Delta H'' \quad (5)$$

is an approximate measure of the heat of dilution part of ΔH_c and $\Delta H''$ is the heat of the reaction $\frac{1}{2}H_2O_2(aq) \longrightarrow \frac{1}{2}H_2O(l) + \frac{1}{4}O_2(g)$ in $(xa + \frac{1}{2}c)H_2O$.[24] Significantly, for the run in which decomposition of hydrogen peroxide was suspected, the apparent value of ΔH_b was more negative than the above, that of ΔH_c more positive, and their sum about the same (−68.69 as opposed to −68.66 kcal mol^{-1}). The heat of formation of the ferrate is given by equation (6) where ΔH_d is

$$\Delta_f H^\circ[K_3FeF_6(c)] = 3\Delta_f H^\circ[KHF_2(c)] + \tfrac{1}{2}\Delta_f H^\circ[H_2O_2 \text{ (in } cH_2O)] - \Delta_f H^\circ[H_2O(l)] - \Delta H_a + \Delta H_b + \Delta H_c - \Delta H_d + \Delta H_e \quad (6)$$

the heat of dilution of $[xHF, xaH_2O]$ with $(\frac{1}{2}c + 1)H_2O$, and $\Delta H_c = \Delta H_3$ above. The value of ΔH_d is calculated to be −11.31 kcal mol^{-1} from the data of Johnson *et al.*[25]

Cobaltate. Two heats of solution were measured: (i) that of the cobaltate in B containing an excess of potassium iodide; (ii) that of cobalt plus KHF_2 in B. Tests had shown that K_3CoF_6 liberates 100—101% of the theoretical amount of iodine when it is rapidly dispersed in a large excess of acidic potassium iodide solution. The results (kcal mol^{-1}) obtained were as follows. The value of ΔH_{ii} (not reported in ref. 5)

$$K_3CoF_6(c) + [wKI, x'H_2SO_4, x'bH_2O] \quad \Delta H_i = -18.05 \text{ [1]}$$

$$Co(c) + 3KHF_2(c) + [x'H_2SO_4, x'bH_2O] \quad \Delta H_{ii} = +7.24 \pm 0.07 \text{ [3]}$$

includes a correction of −0.30 kcal mol^{-1} for evaporation of H_2O with the hydrogen evolved. The heat of formation of the cobaltate was calculated by assuming that (α) the heat of reduction of the solution from (i) with hydrogen is accurately given by the standard heat of reduction $\frac{1}{2}I_3^-(aq) + \frac{1}{2}H_2(g) \xrightarrow{\Delta H_{iii}^\circ} \frac{3}{2}I^-(aq) + H^+(aq)$, and (β) the heat of solution of

* Here and throughout this paper, species enclosed in square brackets represent the composition of a calorimetric solution.

Table 2. Standard enthalpies of formation of the hexafluorometallates(III) at 25 °C, from elements ($\Delta_f H^\ominus$) and gaseous ions (I)

Compound	$\Delta_f H^\ominus$/kcal mol^{-1}	I/kcal mol^{-1}
K_3ScF_6(c)	−797.5	−1 912
K_3TiF_6(c)	−768.0	−1 991
K_3VF_6(c)	−723.2	−2 022
K_3CrF_6(c)	−711.5	−2 064
K_3MnF_6(c)	−680.9	−2 066
K_3FeF_6(c)	−670.9	−2 038
K_3CoF_6(c)	−629.6	−2 086
K_3NiF_6(c)	−611.3	−2 127
K_3CuF_6(c)	−575.4	−2 159
K_3GaF_6(c)	−717.2	−2 108

Table 3. Ligand-field stabilization energies (λ) of the hexafluorometallates(III) as determined from their spectra

Compound	Δ_o/cm^{-1}	λ/kcal mol^{-1}
K_3TiF_6	17 500	20
K_3VF_6	16 200	37
K_3CrF_6	15 600	54
K_3MnF_6	14 100 [a]	37
K_3CoF_6	12 800	15
K_3NiF_6		(33—35) [b]
K_3CuF_6	14 100	48

[a] Calculated on the assumption that the octahedron is elongated, as in K_2NaMnF_6 (ref. 10); δ_e = 9 100 cm^{-1}. [b] Calculated as described in the text.

potassium iodide in the solution from (ii) is the same as its heat of solution in B. These assumptions give equation (7).

$$\Delta_f H^\ominus[K_3CoF_6(c)] = 3\Delta_f H^\ominus[KHF_2(c)] - \Delta H_I + \Delta H_{II} - \Delta H_{III}^\ominus \quad (7)$$

Nickelate. A provisional value for the heat of formation was obtained by comparing the heat of solution of our sample in B with that of the cuprate in approximately the same solvent (see below). The result obtained was ΔH = −3.42 [1] kcal mol^{-1}, as compared with −10.74 kcal mol^{-1} for K_3CuF_6. The heat of formation was calculated from equations (2) and (4).

Cuprate. Two heats of solution were measured: (I) that of the cuprate in B to which some water (0.081 g per 275 g) had been added; (II) that of copper(II) oxide plus KHF_2 in B. The results (kcal mol^{-1}) obtained are given below. The reaction

$$K_3CuF_6(c) + [x'H_2SO_4, (x'b + \tfrac{3}{2})H_2O] \qquad \Delta H_I = -10.74 \pm 0.35 \text{ [3]}$$

$$3KHF_2(c) + CuO(s) + [x'H_2SO_4, x'bH_2O] \qquad \Delta H_{II} = +6.86 \pm 0.25 \text{ [3]}$$

taking place in (I) was assumed to be similar to that between fluorine and dilute sulphuric acid, as reported by Cady.[26] The products were taken to be hydrogen peroxide, accounting for *ca.* 80% of the cuprate, and oxygen, accounting for *ca.* 20%. The corresponding heat of reaction for the formation of 100% oxygen is then given by equation (8) where ΔH is the heat of

$$\Delta H_I' \approx \Delta H_I + 0.8\Delta H \quad (8)$$

decomposition of $\frac{1}{2}H_2O_2$ in $(x'b + \frac{1}{2})H_2O$, 11.31 kcal mol^{-1} (see ref. 24). Further investigation of reaction (I) is desirable. The heat of formation of the cuprate is given by equation (9)

$$\Delta_f H^\ominus[K_3CuF_6(c)] = 3\Delta_f H^\ominus[KHF_2(c)] + \Delta_f H^\ominus[CuO(s)] - \tfrac{3}{2}\Delta_f H^\ominus[H_2O(l)] - \Delta H_I' + \Delta H_{II} - \Delta H_{III} \quad (9)$$

where ΔH_{III} is the heat of dilution of $[x'H_2SO_4, x'bH_2O]$ with $\frac{3}{2}H_2O$. This is calculated to be −0.01 kcal mol^{-1} from ref. 24.

In equation (9), $\Delta_f H^\ominus$[CuO(s)] is the heat of formation of the copper(II) oxide used. From its method of preparation and ease of dissolution in acid, this was taken to be the 'active' form.[27]

Gallate. The same procedure was used as for the scandate. The results obtained were ΔH_1 = −8.21 ± 0.04 [3] and ΔH_2 = −58.69 ± 0.20 [3] kcal mol^{-1}.

Heats of Formation.—The values obtained for $\Delta_f H^\ominus$-[K_3MF_6(c)], and hence for I [equation (1)], are given in Table 2. Ancillary values of $\Delta_f H^\ominus$ were taken from ref. 24 [H_2O(l), I^-(aq), I_3^-(aq), Cu^{2+}(aq)], supplemented with values from refs. 1 [M^{3+}(g)], 28 [H_2O_2(cH_2O), Mn^{2+}(aq), Co^{2+}(aq), Ni^{2+}(aq)], and 29 [K^+(g), F^-(g)]. The value for KHF_2(c) was calculated to be −223.03 kcal mol^{-1} from the heat of dissociation given in ref. 29 and the values for KF(c) and HF(g) given in ref. 24. The value for CuO(s) was taken to be −35.4 kcal mol^{-1} from refs. 27*b* and 29.

The uncertainties in the values in Table 2 are difficult to estimate because systematic errors in thermochemical measurements invariably exceed random errors, and there are no independent measurements of $\Delta_f H^\ominus[K_3MF_6(c)]$ with which to make comparisons. Most of the values, however, should be accurate to within ±5 kcal mol^{-1}, with higher uncertainties only for K_3CoF_6 (±7), K_3CuF_6 (±7), K_3MnF_6 (±10), and K_3NiF_6 (±10).

Optical Spectra and Ligand-field Stabilization Energies.—The diffuse reflectance spectra of the hexafluorometallates(III) were recorded over the range 4 000—42 000 cm^{-1} at room temperature. The results obtained were similar to those reported in the literature,[8,30] except for the positions of the bands in the 20 000—30 000 cm^{-1} region of the spectrum of the chromate. The spectra were interpreted on the basis of ligand-field theory for an octahedral field of intermediate strength, tetragonally distorted in the case of K_3MnF_6, to give the values of the ligand-field splitting parameters Δ_o and δ_e presented in Table 3. Here Δ_o represents the octahedral splitting of the d level and δ_e the splitting of the e_g. The assumption was made that tetragonal distortion does not substantially effect the baricentres of the e_g and t_{2g} levels,[31] contrary to the predictions of the classical, point-charge model.[32] The values in Table 3 are in good agreement with literature values calculated on the same basis.[8,9,30,33] No attempt was made to derive values for K_3NiF_6 from our spectrum of the nickelate because of the impurities in our sample. Other workers, however, have obtained very similar spectra to ours, both for the potassium salt and for other alkali-metal salts, and have succeeded in interpreting them on the basis of a low-spin ground state for the NiF_6^{3-} ion, tetragonally distorted in the same way as for MnF_6^{3-}.[8,9] Allen and Warren [8] use the classical model, but this leads to the unsatisfactory result that the energy gained by elongation of the octahedron is the same for the high-spin state as it is for the low-spin. Reinen *et al.*,[9] however, assume that the baricentres of the e_g and t_{2g} levels are invariant to distortion, and, with the help also of e.s.r. measurements, obtain values for the ligand-field parameters in line with those for the other MF_6^{3-} ions.

Ligand-field stabilization energies were calculated from the splitting parameters by the strong-field formula (10) for the configuration $t_{2g}^p e_g^q$ with the addition of $\frac{1}{2}\delta_e$ for the manga-

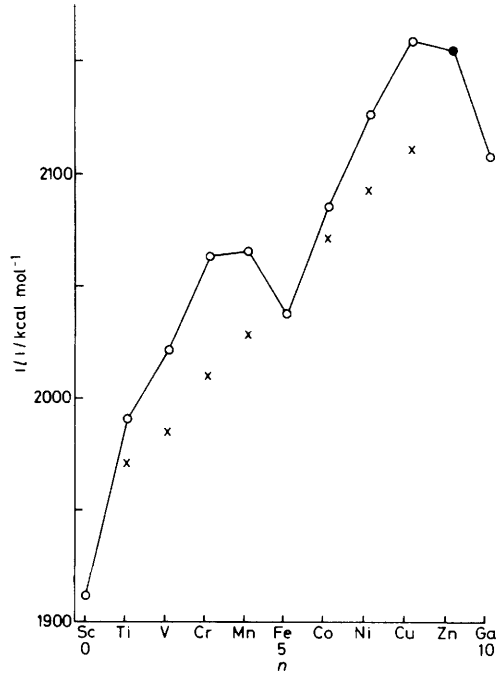

Figure. Plot of $|l|$ for the hexafluorometallates(III) against n, the number of $3d$ electrons on the gaseous M^{3+} ion. ○, Observed values of l; ×, values corrected for ligand-field stabilization energies calculated from spectroscopic data; ●, estimated value

nate. A value for the nickelate was obtained by calculating the stabilization energy of the high-spin state from Reinen

$$\lambda/Nhc = (\tfrac{2}{5}p - \tfrac{3}{5}q)\Delta_o \qquad (10)$$

et al.'s value of Δ_o (14 000 cm^{-1})[9] and adding to this the difference in energy between high- and low-spin forms (d). Reinen *et al.* obtained values of d for several salts, the nearest to K_3NiF_6 being Rb_2KNiF_6, their value for which corresponds to *ca.* 2.8 kcal mol^{-1}. Alter and Hoppe[7c] obtained somewhat lower values from the variation of $\mu_{eff.}$ with temperature, that for K_3NiF_6 being *ca.* 0.8 kcal mol^{-1}.

Discussion

The values of $|l|$ are plotted as a function of the number of $3d$ electrons in the Figure. The familiar double-humped curve is obtained, in general agreement with the predictions of ligand-field theory and the assumption made in ref. 1.

On closer examination, however, the two humps are somewhat bigger than might have been expected. If the spectroscopic values for the ligand-field stabilization energies of the compounds (Table 3) are substracted from $|l|$ in the usual way, the resulting points, instead of falling on a smooth curve as they do for dipositive species,[31] continue to generate two humps (Figure). Relative to a parabolic baseline through the values for $n = 0$, 5, and 10, the values for vanadium and chromium lie 16 kcal mol^{-1} above a smooth curve, while those for nickel and copper lie 20 and 24 kcal mol^{-1} above.

Without further experimental work, it is difficult to be sure whether these residual humps are real or not. They are supported, however, by the corrected heats of hydration of the tripositive ions given by McClure and co-workers,[34,35] which show signs of a similar hump in the first half of the series where data are available. If these humps are real, they raise the question of precisely what kind of curve to expect when quantities like $|l|$ are corrected in this way. George and McClure[35] discussed this issue several years ago, and came to the conclusion that the curve should be slightly double-troughed in shape.[36] They admit, however, that their treatment is oversimplified, and this is borne out by the following, more detailed analysis.

Consider the simple case of an isolated octahedral d^1 system MX_6 at 0 K, executing simple-harmonic vibrations. The ground state of the system (t_{2g}^1) is split by spin–orbit coupling, but we shall assume that the effects of spin–orbit coupling have been suitably corrected for.† The ground-state energy may then be written as in equation (11) where R_e is the equilibrium M–X

$$U(R_e) = F(R_e) - \tfrac{2}{5}\Delta_{et.}(R_e) + E_z \qquad (11)$$

distance, $\Delta_{et.}$ is the splitting of the d level, F is the electronic energy of the system apart from that given by the $\Delta_{et.}$ term, and E_z the zero-point energy. The spectroscopic value of Δ ($\Delta_{spec.}$) is given by the difference between $U(R_e)$ and the energy of the excited state (e_g^1) at the same internuclear distance, $U^*(R_e)$, plus one quantum of an enabling, odd vibration, E_v^*. The energy $U^*(R_e)$ may be written as in equation (12) from

$$U^*(R_e) = F^*(R_e) + \tfrac{3}{5}\Delta_{et.}(R_e) \qquad (12)$$

which we obtain expression (13). Now we are interested in the

$$\Delta_{spec.} = \Delta_{et.}(R_e) + F^*(R_e) - F(R_e) + E_v^* - E_z \qquad (13)$$

hypothetical state of the system in which ligand-field effects are not operating, corresponding to the configuration $t_{2g}^{\frac{6}{5}}e_g^{\frac{4}{5}}$. This has the energy in equation (14) with $R_e^0 > R_e$.[36]

$$U^0(R_e^0) = F^0(R_e^0) + E_z^0 \qquad (14)$$

Thus the true ligand-field stabilization energy is given by equations (15) and (16). Now George and McClure[35] effectively

$$|U(R_e) - U^0(R_e^0)| = \tfrac{2}{5}\Delta_{spec.} + \delta \qquad (15)$$

$$\delta = F^0(R_e^0) - F\tfrac{3}{5}(R_e) - \tfrac{2}{5}F^*(R_e) + E_z^0 - \tfrac{3}{5}E_z - \tfrac{2}{5}E_v^* \qquad (16)$$

assume that $F = F^* = F^0$ and that vibrations can be neglected. These assumptions give $\delta < 0$, but are obviously very approximate. As equation (16) stands, there is no reason why δ, or the corresponding quantity for a crystal at 25 °C, should not be >0.

A further feature of the plot of $|l|$ against n is that, relative to a parabolic baseline through the values for $n = 0$, 5, and 10, the second hump is about the same size as the first (rising to 72 as compared with 70 kcal mol^{-1}), whereas in analogous plots for dipositive species the second hump is distinctly smaller than the first (see Figure 6 of ref. 1). This difference between tripositive and dipositive species, if real, lowers the accuracy of the estimates obtained in ref. 1 for compounds of tripositive cobalt, nickel, copper, and zinc, which are based on the assumption that the relative sizes of the humps are the same in the two oxidation states.

If the values of l in Table 2 are accepted, they can be used to obtain estimates of the enthalpies of formation of other high-spin, or near high-spin, species of cobalt(III), nickel(III), and copper(III) by the method of Karapet'yants.[37] Thus, estimates of the enthalpies of formation of nickel trifluoride and copper

† George and McClure[35] do this by adding to their heats the difference in energy (P^+) between the baricentre of the ground term of the free ion and the lowest level of this term. If we were to do the same, our residual humps would be a little larger {by $P^+ - (H_{298}^\ominus - H_0^\ominus)_{et.}[M^{3+}(g)]$ or up to 3.7 kcal mol^{-1}}. Corrections are also required to allow for spin–orbit coupling within the complex, but these are necessarily smaller.

Table 4. Standard Gibbs free energies of decomposition ($\Delta G^{\ominus}$) of cobalt, nickel, and copper trifluorides at 25 °C

M	$\Delta_f H^{\ominus}[MF_2(c)]$/ kcal mol^{-1}	$\Delta_f H^{\ominus}[MF_3(c)]$/ kcal mol^{-1}	$\Delta G^{\ominus}$/ kcal mol^{-1}
Co	−160.5 [a]	−188.9 [a]	+22.1 [a]
Ni	−157.1 [b]	(−166) [c]	(+2) [d]
Cu	−128.8 [b]	(−125) [c]	(−10) [d]

[a] Ref. 29. [b] W. N. Hubbard, G. K. Johnson, and V. Ya. Leonidov, in 'Combustion Calorimetry,' eds. S. Sunner and M. Månsson, Pergamon, Oxford, 1979, ch. 12. [c] Estimated from a plot of $l(MF_3)$ against l. The values of $l(MF_3)$ were calculated from the following heats of formation by means of equation (7) of ref. 1: $ScF_3(c)$, $CrF_3(c)$, $GaF_3(c)$, ref. 28; $TiF_3(c)$, $CoF_3(c)$, $F^-(g)$, ref. 29; $MnF_3(c)$, −247.6 kcal mol^{-1}, calculated from the heat of dissociation of $MnF_4(c)$ into $MnF_3(c)$ given by T. C. Ehlert and M. Hsia (*J. Fluorine Chem.*, 1972/73, **2**, 33) and the heat of formation of MnF_4-(c) given by R. Hoppe, B. Müller, J. Burgess, R. D. Peacock, and R. Sherry (*J. Fluorine Chem.*, 1980, **16**, 189); $FeF_3(c)$, −237.0 kcal mol^{-1}, the average of the values given by V. S. Pervov, A. G. Muravina, and S. A. Ryabov [*Dokl. Phys. Chem. (Engl. Transl.)*, 1981, **257**, 229] and G. K. Johnson (*J. Chem. Thermodyn.*, 1981, **13**, 465); $M^{3+}(g)$, ref. 1. A reasonably good correlation was obtained, deviations from linearity being <5 kcal mol^{-1}. A value was also derived for $VF_3(c)$ of −295 kcal mol^{-1}. [d] Calculated by means of equations (2) and (12) of ref. 1, with $\Delta S^{\ominus} \approx 22$ cal K^{-1} mol^{-1} from ref. 38. Estimated uncertainty ±10—15 kcal mol^{-1}.

trifluoride can be obtained by plotting $l(MF_3)$ against l, where $l(MF_3)$ is the lattice enthalpy of MF_3. From these can be calculated the free energies of the decompositions $MF_3(c) \longrightarrow MF_2(c) + \frac{1}{2}F_2(g)$. The results are given in Table 4, where they are compared with the corresponding data for cobalt trifluoride. The figures suggest that nickel trifluoride might just be stable enough to dissociation under ordinary conditions to be prepared. This prediction has been put to the test by Court and Dove,[17] who succeeded in making NiF_3 by treating K_2NiF_6 with AsF_5 in liquid HF.

To complete the Figure, a value of l was estimated for K_3ZnF_6. The value chosen (−2 155 kcal mol^{-1}) was a compromise between that obtained by adding $l(K_3MnF_6) - l(K_3CrF_6)$ to $l(K_3CuF_6)$ (−2 161 kcal mol^{-1}) and the value obtained by adding $l(K_3MnF_6) - \frac{1}{2}[l(K_3CrF_6) + l(K_3FeF_6)]$ to $\frac{1}{2}[l(K_3CuF_6) + l(K_3GaF_6)]$ (−2 148 kcal mol^{-1}). The value of −2 155 kcal mol^{-1} gives $\Delta_f H^{\ominus}[K_3ZnF_6(c)] \approx -570$ kcal mol^{-1}, which, with a value of −468 kcal mol^{-1} for $\Delta_f H^{\ominus}[K_2ZnF_4(c)]$ estimated from that for $\Delta_f H^{\ominus}[KZnF_3(c)]$,[28] and an estimated value of 22 cal K^{-1} mol^{-1} for the entropy change,[38] gives $\Delta G^{\ominus} \approx -41$ kcal mol^{-1} for the decomposition $K_3ZnF_6(c) \longrightarrow K_2ZnF_4(c) + KF(c) + \frac{1}{2}F_2(g)$ at 25 °C. The increasing tendency of the hexafluorometallates(III) beyond iron to decompose by loss of fluorine apparently becomes intolerable just as the dipositive state completes its shell.

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