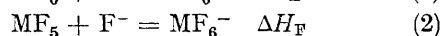
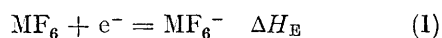


Thermochemistry of Alkali Metal Hexafluoromolybdates(v) and Hexafluorotungstates(v)

By John Burgess, Ian Haigh, Raymond D. Peacock,* and Paul Taylor, Department of Chemistry, University of Leicester, Leicester LE1 7RH

From measurements of the respective heats of alkaline hypochlorite hydrolysis at 298 K, the standard enthalpies of formation of KWF_6 , RbWF_6 , CsWF_6 , KMoF_6 , RbMoF_6 , and CsMoF_6 have been derived. They are -2224 ± 6 , -2236 ± 9 , -2258 ± 6 , -2075 ± 9 , -2099 ± 8 , and $-2117 \pm 7 \text{ kJ mol}^{-1}$ respectively. Values for the electron affinities (ΔH_E) of gaseous tungsten hexafluoride and molybdenum hexafluoride have thence been estimated as $\Delta H_E[\text{WF}_6(\text{g})] = -490 \pm 5$ and $\Delta H_E[\text{MoF}_6(\text{g})] = -517 \pm 6 \text{ kJ mol}^{-1}$, at 298 K. For the reactions $\text{MF}_5(\text{g}) + \text{F}^-(\text{g}) \longrightarrow \text{MF}_6^-(\text{g})$ the fluoride ion affinities (ΔH_F) of tungsten pentafluoride and molybdenum pentafluoride are estimated to be -491 ± 5 and $-412 \pm 6 \text{ kJ mol}^{-1}$ respectively.

FEW thermochemical data for complex fluorides are available. Present information is insufficient either to enable estimates of the stabilities of known complex fluorides to be made, or to allow the calculation of derived data such as electron affinities [equation (1)] and fluoride ion affinities [equation (2)]. Knowledge of these affinities would be useful in predicting the possible existence and reactions of as yet unknown compounds.



Qualitative estimates of the minimum values of electron

¹ N. Bartlett, *Angew. Chem. Internat. Edn.*, 1968, **7**, 433.

² G. C. Goode, Ph.D. Thesis, University of Aston, 1969, pp. 45–47.

affinities of a number of transition metal hexafluorides, based upon the reactivity of the hexafluorides towards oxidisable molecules such as nitric oxide, nitrogen dioxide, or oxygen, have been made by Bartlett¹ with values ranging from $\Delta H_E = -90 \text{ kcal mol}^{-1}$ for ReF_6 to $-156 \text{ kcal mol}^{-1}$ for PtF_6 . Magnetron experiments, in which the equilibrium $\text{MF}_6 + \text{e}^- \rightleftharpoons \text{MF}_6^-$ is set up and monitored at a heated metal surface, led to a surprisingly small estimate for ΔH_E of $-68.2 \text{ kcal mol}^{-1}$ for the electron affinity of WF_6 .²

Studies³ of the chemical reactions of molybdenum and tungsten hexafluorides with lower fluorides of non-

³ T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 1966, **5**, 1434; J. R. Geichmann, E. A. Smith, S. S. Trond, and P. R. Ogle, *ibid.*, 1962, **1**, 661.

metallic elements, nitric oxide, and nitrosyl chloride have illustrated the relative inertness of tungsten hexafluoride. Hammond⁴⁻⁶ has suggested, from a study of band positions in the charge-transfer spectra of these hexafluorides with organic donors, that the molecular electron affinity of molybdenum hexafluoride is greater than that of tungsten hexafluoride.

In a preliminary communication from this laboratory,⁷ the heat of alkaline oxidative hydrolysis of KWF_6 was reported, and a value of $\Delta H_{\text{E}} = \text{ca. } -120 \text{ kcal mol}^{-1}$ (-500 kJ mol^{-1}) was estimated for the electron affinity of tungsten hexafluoride. We have now measured the heats of oxidative alkaline hydrolysis of the potassium, rubidium, and caesium salts of the hexafluoromolybdate(v) and hexafluorotungstate(v) anions, and thence calculated values for the heats of formation of these compounds and for the respective hexafluorometallate

TABLE 1

Unit cell dimensions of potassium, rubidium, and caesium hexafluoromolybdates(v) and hexafluorotungstates(v)

Compound	Unit cell parameters/Å	$r_0/\text{Å}^*$
KWF_6	$a_0 = 10.21, c_0 = 10.09$	4.40 ₅
RbWF_6	$a_0 = 5.14 (\alpha_0 = 97.3^\circ)$	4.42 ₅
CsWF_6	$a_0 = 5.31 (\alpha_0 = 95.3^\circ)$	4.57 ₀
KMoF_6	$a_0 = 10.17, c_0 = 9.97$	4.37 ₅
RbMoF_6	$a_0 = 5.11 (\alpha_0 = 96.5^\circ)$	4.39 ₉
CSMoF_6	$a_0 = 5.29 (\alpha_0 = 96.0^\circ)$	4.54 ₉

* Unit length, defined in text.

anions. From the results we have deduced the electron affinities of the hexafluorides, and the fluoride ion affinities of the pentafluorides, of molybdenum and tungsten.

published earlier.⁸ The presence of the hexafluorotungstate(v) ion ($\nu_3 = 594 \text{ cm}^{-1}$)⁸ and the hexafluoromolybdate(v) ion ($\nu_3 = 615 \text{ cm}^{-1}$)⁸ in each sample was confirmed by i.r. spectra recorded on a Perkin-Elmer 225 spectrometer. For each salt the alkali metal was determined by precipitation with sodium tetraphenylborate;⁹ tungsten was precipitated as the tannin-cinchonine complex, ignited and weighed as the trioxide;¹⁰ and molybdenum was estimated as the oxine derivative as appropriate.⁹ The analyses are recorded in Table 2.

Calorimetry.—The calorimeter was a modified version of the one described by Myers and Brady,¹¹ and was operated at 298.2 K. A frangible glass bulb containing a known mass (between 0.13 and 0.21 g) of the compound was broken into 150 cm³ of a solution of sodium hydroxide (0.1M) and sodium hypochlorite (1.5%) contained in a glass Dewar. The temperature change of the calorimeter's contents was followed by a thermistor (Type F-23 supplied by Standard Telephone and Cable Company Limited), whose changing resistance was monitored by a Kipp-Zonen BD 5 recorder incorporated in a Wheatstone bridge circuit. The recorder was calibrated by supplying a known amount of current through a constantan wire of known resistance for a specified time. The performance of the calorimeter was periodically checked by standardisation with tris(hydroxymethyl)-methylamine.¹²

RESULTS

Three heats of hydrolysis were recorded for each of two individual samples, yielding a total of six results, for each compound. The experimental calorimeter results are summarised in Table 2. The hydrolysis of AMoF_6 and AWF_6 ($A = \text{K, Rb, Cs}$) by alkaline hypochlorite solution occurs quantitatively according to equation (3), with $A = \text{K, Rb,}$

TABLE 2
Analyses and thermochemical results for AMoF_6 and AWF_6 series

Compound	Analyses/%					Mean ΔH_{hydr}^a /kJ mol ⁻¹	σ^b /kJ mol ⁻¹	ΔH_f° (298) /kJ mol ⁻¹
	Alkali metal		W or Mo		No. of hydrolyses			
	Found	Calc.	Found	Calc.				
KWF ₆	11.4	11.6	54.9	54.6	6	-517	6	-2224
RbWF ₆	22.3	22.2	47.8	48.0	6	-505	9	-2236
CsWF ₆	30.3	30.9	42.8	42.7	6	-495	6	-2258
KMoF ₆	16.1	15.7	38.1	38.5	6	-592	9	-2083
RbMoF ₆	28.9	29.5	32.7	32.5	6	-577	8	-2099
CsMoF ₆	39.1	38.7	27.7	28.0	6	-569	7	-2117

^a Heat of alkaline hypochlorite hydrolysis. ^b Standard deviations, from which standard errors of the means and their confidence limits can be calculated by standard procedures (see, e.g., E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7-9).

EXPERIMENTAL

Preparations.—The compounds AWF_6 and AMoF_6 ($A = \text{K, Rb, Cs}$) were prepared by established procedures.⁸ From X-ray diffraction patterns (Debye-Scherrer), the lattice constants (Table 1) were derived for each compound. These values show satisfactory agreement with those

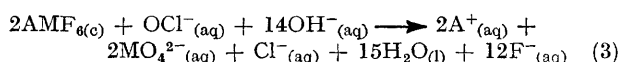
* Standard enthalpies of formation have been taken from the sources cited in the previous paper, plus D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge, 1968, pp. 208-216 [$\text{K}^+(\text{g})$, $\text{Rb}^+(\text{g})$, $\text{Cs}^+(\text{g})$, and $\text{F}^-(\text{g})$]; J. Schröder and F. J. Sieben, *Chem. Ber.*, 1970, **103**, 76 [$\text{WF}_6(\text{g})$ and $\text{WF}_6(\text{c})$]; and I. Haigh, Ph.D. Thesis, Leicester, 1973 [$\Delta H_f^\circ[\text{MoF}_6(\text{c})] = 331 \text{ kcal mol}^{-1}$].

⁴ P. R. Hammond, *J. Phys. Chem.*, 1970, **74**, 647.

⁵ P. R. Hammond and R. R. Lake, *Chem. Comm.*, 1968, 987.

⁶ P. R. Hammond and W. S. McEwan, *J. Chem. Soc. (A)*, 1971, 3812.

or Cs, and $M = \text{Mo or W}$. The standard enthalpy of formation of (ΔH_f°) of each compound was calculated from the



heat of hydrolysis and the appropriate ancillary thermochemical data.* The results are incorporated in Table 2.

⁷ J. Burgess, I. Haigh, and R. D. Peacock, *Chem. Comm.*, 1971, 977.

⁸ G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1957, 4212.

⁹ A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

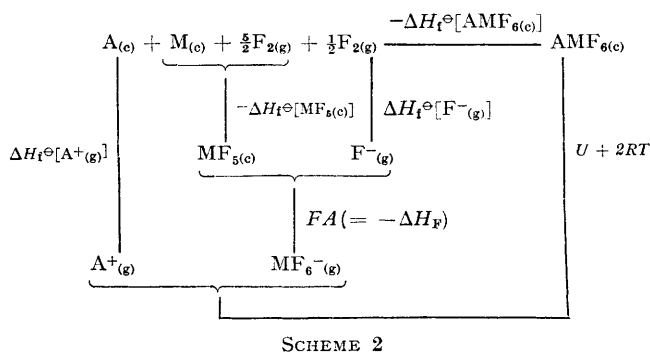
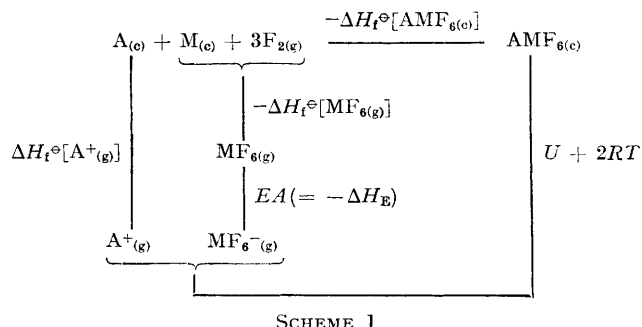
¹⁰ D. A. Lambie, *Analyst*, 1945, **70**, 124.

¹¹ O. E. Myers and A. P. Brady, *J. Phys. Chem.*, 1960, **64**, 591.

¹² J. O. Hill, G. Öjelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111.

DISCUSSION

The main purpose of this work has been to obtain estimates for the electron affinities of the hexafluorides and the fluoride ion affinities of the pentafluorides. These quantities may be obtained,* *via* enthalpies of formation of the gaseous MF_6^- ions, from the thermochemical data of Table 2 and the lattice enthalpies of the respective salts. The thermochemical cycles used are shown in Schemes 1 and 2; lattice energies (U) can be



calculated from the known structures.⁸ All six salts have distorted caesium chloride structures with the alkali metal and transition metal ions occupying the caesium and chloride positions respectively. The potassium salts have a tetragonal modification with either 4 or 8 molecules in the unit cell; the rubidium and caesium salts are rhombohedrally distorted with 1 molecule in the unit cell. These distortions are not large, but they could lead to a significant lowering of the Madelung constant. A further reduction of the lattice energy could be caused by the (almost certain) presence of partial charges on the fluorine and transition metal atoms leading to multipole interactions. For the present purpose, the simplest assumption has been made, *viz.* that the lowering of the lattice energy from these causes will be balanced by the van der Waals forces, which lead to an increase in the lattice energy and which are likely to be significant in these complex salts. This is close to the Kapustinskii assumptions¹³ and is illustrated by recent calculations¹⁴ of the lattice energies of the complex chlorides K_2TeCl_6 and K_2SnCl_6 , where the gross cancellation of errors is clearly shown. We have

* Our values for electron affinities and fluoride ion affinities are at 298 K, not, as they should ideally be, at 0 K. While we have, or can extrapolate, values for some of our thermochemical quantities at 0 K, this is not the case for others.

therefore used the normal Born-Meyer expression [equation (4)], with the cube root of the volume of one formula unit as the unit length (r_0), and a ρ value of

$$U = \frac{N_0 A z_1 z_2 e^2}{r_0} \left(1 - \frac{\rho}{r_0} \right) \quad (4)$$

0.345. The resultant lattice energies, calculated from the crystal parameters of Table 1, are listed in Table 3.

TABLE 3

Estimated lattice energies (U_{298}) of AMF_6 salts

	$U_{298}/\text{kJ mol}^{-1}$		$U_{298}/\text{kJ mol}^{-1}$
KWF_6	-531	KMoF_6	-535
RbWF_6	-520	RbMoF_6	-525
CsWF_6	-504	CsMoF_6	-507

The assumptions are at least partly justified by the consistency of the calculations of the enthalpies of formation of the anions, of electron affinities, and of fluoride ion affinities (Table 4). The results indicate that the

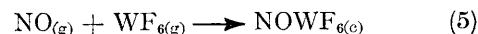
TABLE 4

Enthalpies of formation of MF_6^- anions, electron affinities of MF_6 , and fluoride ion affinities of MF_5 , for $M = \text{W}$ or Mo

Compound	$\Delta H_f^0[\text{MF}_6^-(\text{g})]/\text{kJ mol}^{-1}$	$\Delta H_E[\text{MF}_6(\text{g})]/\text{kJ mol}^{-1}$	$\Delta H_F[\text{MF}_5(\text{c})]/\text{kJ mol}^{-1}$
KWF_6	-2209	-487	-488
RbWF_6	-2213	-491	-492
CsWF_6	-2213	-493	-494
Mean	-2212 ± 5^a	-490 ± 5^a	-491 ± 5^a
KMoF_6	-2063	-512	-407
RbMoF_6	-2070	-520	-415
CsMoF_6	-2070	-519	-414
Mean	-2068 ± 6^a	-517 ± 6^a	-412 ± 6^a

^a Standard deviation.

electron affinity of MoF_6 is greater (more exothermic) than that of WF_6 by *ca.* 30 kJ mol^{-1} , in accordance with the difference in observed chemical properties, but that WF_5 is a considerably better fluoride ion acceptor than MoF_5 (*ca.* 80 kJ mol^{-1} difference). It should be noted that as the heats of formation of gaseous MoF_5 and WF_5 are not known, the fluoride ion affinities refer to $\text{MF}_{5(\text{c})}$ and not, more conventionally, to gaseous pentafluoride. Interestingly, the reported lack of reaction¹ between NO and WF_6 is borne out by the present observations. If it is assumed that NOWF_6 has the CsCl type of structure proposed for NOMoF_6 ,³ then it can easily be estimated that for the reaction shown in equation (5) ΔG_{298} is positive to the extent of *ca.* 20 kJ mol^{-1} .



The two fluoride ion affinities of $\Delta H_F = -414 \text{ kJ mol}^{-1}$ for $\text{MoF}_{5(\text{c})}$ and $\Delta H_F = -494 \text{ kJ mol}^{-1}$ for $\text{WF}_{5(\text{g})}$ may be compared with the only other fluoride ion affinity available, *viz.*, that of $\Delta H_F = -385 \text{ kJ mol}^{-1}$ for $\text{BF}_{3(\text{g})}$.¹⁵ Clearly, these are of the same order, and it is possible, so far as the gaseous molecules are concerned, that BF_3 would be at least as good a fluoride ion acceptor as WF_5 .

[3/1776 Received, 24th August, 1973]

¹³ A. F. Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.

¹⁴ M. Webster and P. H. Collins, *J.C.S. Dalton*, 1973, 588.

¹⁵ J. L. Bills and F. A. Cotton, *J. Phys. Chem.*, 1960, **64**, 1477.