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THE FLUORIDE ION AFFINITY OF TUNGSTEN PENTAFLUORIDE AND THE ELECTRON AFFINITY OF TUNGSTEN HEXAFLUORIDE.

J. BURGESS and R. D. PEACOCK

Chemistry Department, University of Leicester, Leicester LE1 7RH
(Great Britain)

SUMMARY

Enthalpies of oxidative alkaline hydrolysis of the salts $LiWF_6$ and $NaWF_6$ are -549 and -519 kJ mol^{-1} respectively. From these results and earlier thermochemical results for KWF_6, $RbWF_6$, and $CsWF_6$, and from crystal structure data for these salts, it has proved possible to assess the charge distribution within the WF_6^- anion in these salts, and to estimate the fluoride ion affinity of WF_5 and the electron affinity of WF_6.

INTRODUCTION

It is possible to estimate the halide ion affinity, ΔH_X, of a metal pentahalide:

$$MX_5 + X^- = MX_6^- \qquad \Delta H_X$$

and the electron affinity, ΔH_E, of a metal hexahalide:

$$MX_6 + e^- = MX_6^- \qquad \Delta H_E$$

from calorimetrically determined enthalpies of formation of these compounds and of hexahalogeno-salts AMX_6. Such estimates require a knowledge of the lattice energy (enthalpy) of the salts AMX_6. Lattice energies are not easy to calculate for salts of polyatomic ions, as both the geometry and the charge distribution within the ion need to be known in order to obtain accurate values. We have previously estimated the electron affinity of tungsten hexafluoride firstly from thermochemical results on potassium hexafluorotungstate(V) [1] and then from results for the rubidium and caesium salts as well [2]. In these papers we used the simple Born-Mayer equation for estimating lattice energies of these salts. The consistency between the estimates from the three salts gave us some confidence in the resulting affinities. However these three salts all have similar nearly cubic structures with the metal ions in a CsCl-type lattice; the potassium salt is a tetragonal modification, the rubidium and caesium salts rhombohedral modifications. In the present paper we report an extension of our investigation to the sodium and lithium salts. These have simple cubic and rhombohedral structures respectively, with the metal atoms in an NaCl-type lattice. This extension gives a useful range of structural types, and in this paper we show how it is possible to obtain an estimate of the charge distribution within the hexafluorotungstate anion, and more acceptable estimates of the fluoride ion affinity of tungsten pentafluoride and the electron affinity of tungste hexafluoride than hitherto.

RESULTS AND DISCUSSION

Our thermochemical results for the oxidative hydrolysis of lithium and sodium hexafluorotungstates(V) are shown in Table 1. In Table 2 we list the ancillary data used to calculate standard enthalpies of formation of these hexafluorotungstate(V) salts (cf. equation (3)). We have recalculated

$$2AWF_6(c) + ClO^-(aq) + 14OH^-(aq) \overset{\Delta H_{hydr}}{=} 2A^+(aq) + 2WO_4^{2-}(aq) + Cl^-(aq) + 12F^-(aq) + 7H_2O(\ell) \qquad (3)$$

enthalpies of formation of the potassium, rubidium, and caesium salts from our original enthalpies of hydrolysis [2] and the Table 2 ancillary data to take account of the various small changes in basic thermochemical data since our original calculations. Enthalpies of formation of the five salts are collected in Table 3, which also reports the appropriate parameters to define their respective crystal structures.

TABLE 1

Thermochemical results for oxidative hydrolysis of hexafluorotungstates(V)

Compound	No. of samples	No. of hydrolyses	Mean ΔH_{hydr}[a] /kJ mol^{-1}	90% confidence limits [3]
$LiWF_6$	2	12	-549 ± 14	± 7
$NaWF_6$	2	7	-519 ± 9	± 7

[a] The error limits cited here are the standard deviations.

TABLE 2

Ancillary thermochemical data used in the derivation of standard enthalpies of formation of hexahalogenotungstates(V) from Table 1

Species	$\Delta H_f^{\ominus}$	Ref.	Species	$\Delta H_f^{\ominus}$	Ref.
$Li^+(aq)$	-278.5	[4]	$F^-(aq)$	-332.6	[5,6]
$Na^+(aq)$	-240.3	[4]	$Cl^-(aq)$	-167.1	[4]
$K^+(aq)$	-252.2	[4]	$WO_4^{2-}(aq)$	-1073.2	[7]
$Rb^+(aq)$	-251.1	[4]	$ClO^-(aq)$	-107.1	[8]
$Cs^+(aq)$	-258.0	[4]	$OH^-(aq)$	-230.0	[5]
			$H_2O(\ell)$	-285.8	[5]

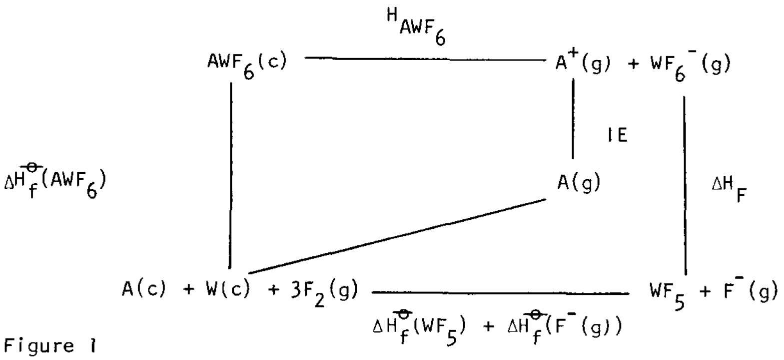


Figure 1

TABLE 3

Enthalpies of formation and crystal parameters for alkali metal hexafluorotungstates(V)

Compound	$\Delta H_f^{\ominus}$ /kJ mol^{-1}	ΔH_o[a] /kJ mol^{-1}	Unit cell parameters /Å
$LiWF_6$	-2219	-152.3 rhombohedral (hexagonal)	$a_o = 5.234$, $c_o = 13.61$
$NaWF_6$	-2211	-183.0 cubic	$a_o = 8.18$[b] [b]
KWF_6	-2224	-202.7 tetragonal	$a_o = 10.21$, $c_o = 10.09$[b]
$RbWF_6$	-2236	-223.1 rhombohedral	$a_o = 5.14$ ($\alpha_o = 97.3^{\circ}$)[b]
$CsWF_6$	-2253	-245.2 rhombohedral	$a_o = 5.31$ ($\alpha_o = 95.3^{\circ}$)[b]

[a] ΔH_o refers to the enthalpy of formation from $AF_{(c)}$ and $WF_{5(c)}$

[b] G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., (1957) 4212.

From the thermochemical cycle it is apparent that there are two unknowns, viz. the fluoride ion affinity, ΔH_F, and the lattice enthalpy of the complex salt, H_{AWF_6}. Of these, ΔH_F is constant, but H_{AWF_6} depends not only upon the nature of A but on the charge distribution within the WF_6^- anion. In our earlier paper we assumed a spherical distribution of charge about the anion, i.e. that the negative charge could be considered to be a point charge on the tungsten atom. This is a satisfactory model for the K, Rb, and Cs salts, but is clearly less satisfactory (Table 4) for the Li and Na salts. It is also possible to use Kapustinskii's equation to derive a thermochemical radius for the anion and an arbitrary value for ΔH_F, which are useful for calculations but are probably of little real significance; here we calculate ΔH_F to be -380 kJ mol^{-1} and the thermochemical radius of WF_6^- to be 2.00Å.

It has now proved possible to make a study of the variation of lattice energy of the hexafluorotungstates(V) with the charge distribution within the WF_6^- ion, calculating the coulombic energies from a computer programme kindly supplied by Professor T. C. Waddington. Using

TABLE 4

Spherical ion model for fluoride ion affinities of alkali hexafluorotungstates(V)

Compound	Lattice Enthalpy (kJ mol^{-1})	ΔH_F (kJ mol^{-1})
$LiWF_6$	-583	-608
$NaWF_6$	-542	-560
KWF_6	-531	-489
$RbWF_6$	-523	-479
$CsWF_6$	-500	-475

TABLE 5

Assumed symmetries, structure types, and tungsten-fluorine distances for alkali metal hexafluorotungstates(V) and for WF_6^-(g)

Compound	Structure type	Space Group	W-F separation(Å)
$LiWF_6$	$LiSbF_6$[a]	C_{3i}^2 - $R\bar{3}$	1.89
$NaWF_6$	$NaTaF_6$[b]	O_h^5 - Fm3m	1.88
KWF_6	$KSbF_6$[c]	C_{4h}^2 - $P\bar{4}2m$	1.83
$CsWF_6$	$CsOsF_6$[d]	C_{3i}^2 - $R\bar{3}$	1.83
$WF_{6(g)}$	Octahedral	-	1.83

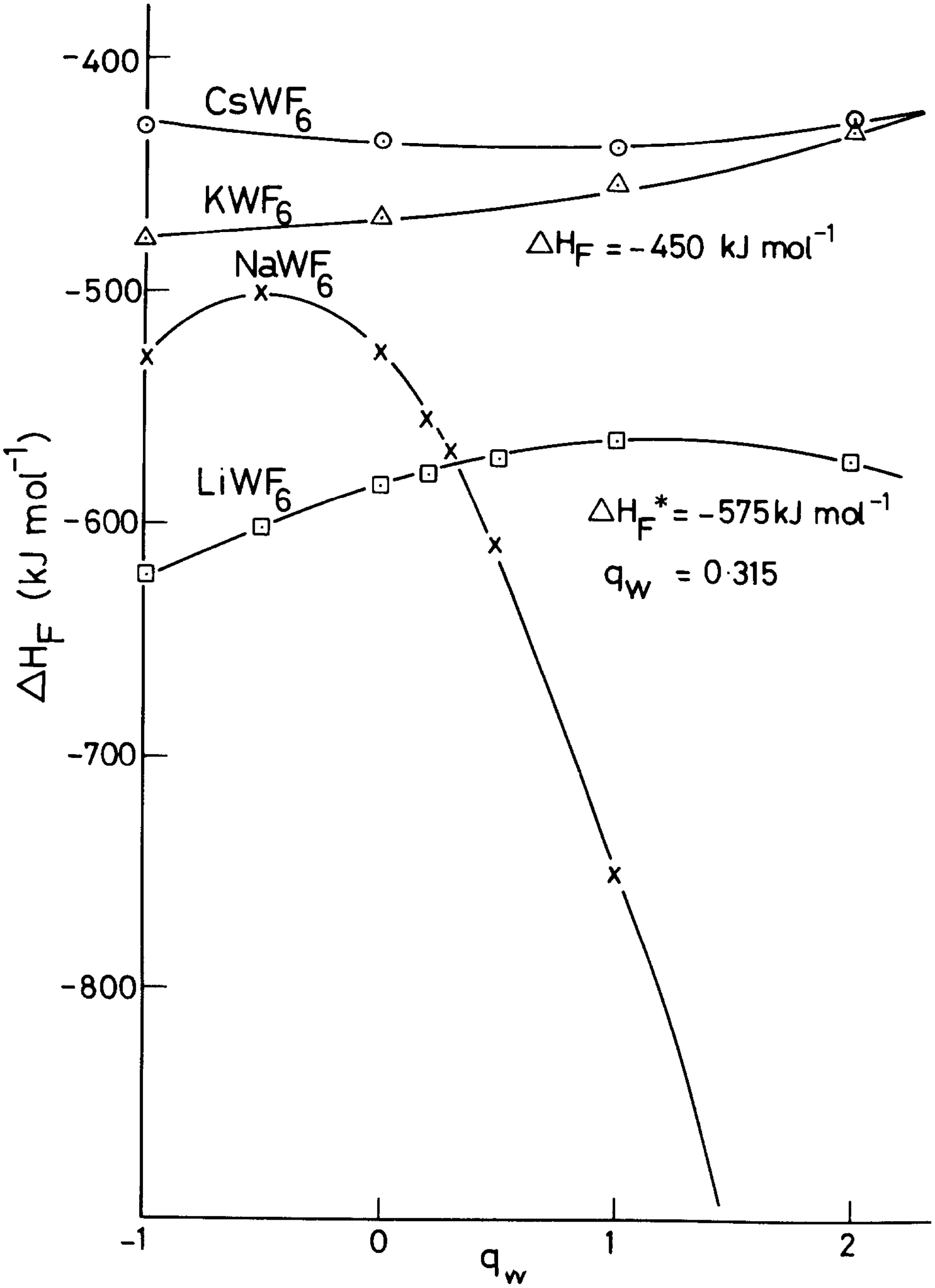
Sources of Table 5 structures:

[a] J. Burns, Acta Cryst., 15 (1962) 1098

[b] J. Fawcett and D. R. Russell, personal communication

[c] G. J. Kruger, C. W. F.T. Pistorius, and A. M.Heyns, Acta Cryst., B32 (1976) 2916

[d] M. A. Hepworth, K. H. Jack, and G. J. Westland, J. Inorg. Nuclear Chem., 2 (1956) 79.


CsWF$_6$
KWF$_6$
NaWF$_6$
LiWF$_6$
$\Delta H_F = -450$ kJ mol^{-1}
$\Delta H_F^* = -575$ kJ mol^{-1}
$q_W = 0{\cdot}315$
ΔH_F (kJ mol^{-1})
-400
-500
-600
-700
-800
-1
0
1
2
q_w

the structural assumptions in Table 5, and plausible short range repulsion energies and van der Waals energies, a plot of the apparent fluoride ion affinity against the charge on the tungsten atom $\underline{a}_w$, for the different salts is obtained (Fig. 2). Several features of this graph are important. Firstly, the variation in lattice enthalpy, and hence ΔH_F, is small for the K and Cs salts. Secondly, the cross-over point on the $LiWF_6$ and $NaWF_6$ points represents the real charge on the tungsten atom, about +0.3. Thirdly, the vertical distance between the cross-over point and the midpoint of the KWF_6 - $CsWF_6$ plots represents the energy needed to expand the WF_6^- anion from W-F = 1.83Å to W-F = 1.89Å. Finally, the assumptions lead to a value of -450 kJ mol^{-1} for ΔH_F. Using the subsidiary cycle shown in Figure 3, which relates the fluoride affinity of WF_5 to the electron affinity of WF_6, and a value of -274 kJ mol^{-1} for the enthalpy of reaction of WF_5(c) with fluorine, $\Delta H_E(WF_6(c))$ is -447 kJ mol^{-1}.

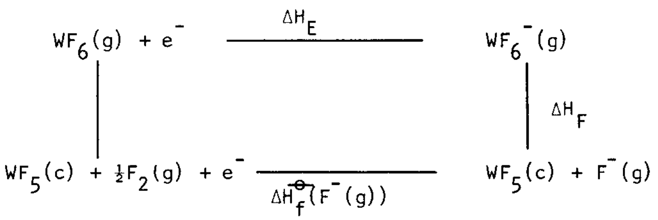


Figure 3

This figure should be compared with values of -434 kJ mol^{-1} derived from a crossed beam experiment [9] and of -356 kJ mol^{-1} from collision ionisation [10], and would tend, within the limits of the assumptions, to confirm the former. Clearly it is now important that the structures of the fluorotungstates should be determined fully, and that methods for calculating the close-range repulsion term in the lattice energies should be estimated from cubic [11] to non-cubic systems so that better estimates may be made.

EXPERIMENTAL

Preparation of $LiWF_6$ and $NaWF_6$

These were prepared by reaction of the dry alkali metal iodides with excess of tungsten hexafluoride in liquid sulphur dioxide solvent [11]. The purity was checked by X-ray powder photography and by i.r. spectroscopy.

Calorimetry

Enthalpies of hydrolysis were measured using the same apparatus and techniques as described previously [2].

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