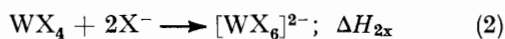
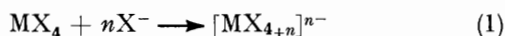


## Thermochemistry of Alkali-metal Hexachloro- and Hexabromo-tungstates(IV) and -rhenates(IV)

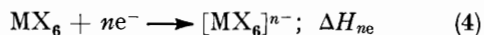
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Enthalpies of hydrolysis or of oxidative hydrolysis are reported for the hexahalogenometallates(IV)  $K_2[WCl_6]$ ,  $K_2[WBr_6]$ ,  $Rb_2[WBr_6]$ ,  $Cs_2[WBr_6]$ ,  $K_2[ReCl_6]$ , and  $K_2[ReBr_6]$ , and for  $ReCl_4$  and  $ReBr_4$ . Enthalpies of formation of these compounds have been calculated from these hydrolysis results. Halide-ion affinities of  $WCl_6$ ,  $WBr_6$ ,  $ReCl_4$ , and  $ReBr_4$ , and two-electron affinities of  $WCl_6$  and  $WBr_6$ , have been estimated from these and other thermochemical results. These estimates have been made using the new direct-minimisation method of Jenkins and Pratt based on the Huggins and Mayer potential to assign the lattice energies of the hexahalogenometallate salts involved.

ENTHALPIES of reaction of tetrahalides with halide ions [equation (1)] can be estimated from the enthalpies of formation of the reactants and products. It is often possible to obtain enthalpies of formation of tetrahalides and of halogeno-anions from calorimetric determinations of the enthalpies of hydrolysis of appropriate compounds; enthalpies of formation of halide ions are well established. In the present paper we report enthalpies of (oxidative) hydrolysis of several salts of hexahalogenometallates(IV), specifically of  $K_2[WCl_6]$ ,  $K_2[WBr_6]$ ,  $Rb_2[WBr_6]$ ,  $Cs_2[WBr_6]$ ,  $K_2[ReCl_6]$ , and  $K_2[ReBr_6]$ , and of rhenium tetrachloride and rhenium tetrabromide. From these results and published thermochemical data we have estimated halide-ion affinities of the respective tetrahalides,  $\Delta H_{2x}$  [equations (2) and (3),  $X = Cl$  or  $Br$ ].†



When the enthalpies of formation both of a hexahalogenometallate and of the parent hexahalide are known, then the  $n$ -electron affinity,  $\Delta H_{ne}$ , of the hexahalide can be deduced [equation (4)].† Since the enthal-



pies of formation of the hexachloride and hexabromide of tungsten are known, we have been able to estimate two-electron affinities of these compounds [equation (4);  $M = W$ ,  $X = Cl$  or  $Br$ ,  $n = 2$ ] from our thermochemical results. For rhenium hexachloride, whose existence<sup>1</sup> requires confirmation, we derive an estimate for the two-electron affinity based on an assumed value for the enthalpy of formation of this compound.

† Strictly these quantities should refer to gas-phase species. However, it is not always possible, due to lack of knowledge on enthalpies of sublimation or of vaporisation, to calculate halide-ion affinities and electron affinities for the gas phase. In such cases these affinities have to be referred to the solid or liquid state. Indeed, for the practising chemist, the halide-ion affinity of a solid or liquid halide may be a more useful guide than the thermodynamically ideal gas-phase value. We shall indicate in the text the phases of the species involved in the halide-ion and electron affinities we quote.

### EXPERIMENTAL

*Preparations.*—The compounds  $K_2[WCl_6]$ ,<sup>2</sup>  $K_2[WBr_6]$ ,<sup>2</sup>  $Rb_2[WBr_6]$ ,<sup>2</sup>  $Cs_2[WBr_6]$ ,<sup>2</sup>  $K_2[ReCl_6]$ ,<sup>3</sup> and  $K_2[ReBr_6]$ <sup>3</sup> were prepared by published methods. Their purity was established by standard analytical procedures (see below), and their lattice constants determined or checked from their X-ray diffraction patterns (Debye-Scherrer).

Samples of rhenium tetrachloride were prepared by the reaction of rhenium metal with antimony pentachloride<sup>4</sup> or by the reaction of rhenium pentachloride, itself prepared from rhenium metal and chlorine,<sup>5</sup> with antimony trichloride.<sup>4</sup> Rhenium tetrabromide was prepared<sup>6</sup> by the dissolution of rhenium dioxide in concentrated hydrobromic acid, followed by evaporation to small volume. The resulting concentrated solution was dried in a desiccator over potassium hydroxide and phosphorus pentoxide.

The compositions of the hexahalogenometallates and of the tetrahalides were confirmed by the following analytical methods. Tungsten was determined by precipitation of the cinchonine-tannin complex and ignition of this to tungsten trioxide.<sup>7</sup> Rhenium was estimated gravimetrically as tetraphenylarsonium tetraoxorhenate(VII).<sup>8</sup> Chloride and bromide were determined by precipitation of their silver salts.<sup>9</sup>

*Calorimetry.*—Two calorimeters were employed, the first a modified version of a calorimeter described by Myers and Brady,<sup>10</sup> the second a standard LKB model 8700 precision calorimeter. Either calorimeter could be incorporated into a Wheatstone bridge circuit, constructed in these laboratories, employing a Kipp-Zonen BD5 recorder as monitor. Both calorimeters were operated at 298.2 K. Both calorimetric assemblies were checked periodically against the well established enthalpies of solution of potassium chloride in water<sup>11</sup> or of neutralisation of tris(hydroxymethyl)methylamine.<sup>12</sup> The number of independently prepared samples of each compound, and the hydrolysis conditions in the calorimeters, are indicated in Table 1. Sample weights of 0.1–0.2 g were hydrolysed in 100 or 150 cm<sup>3</sup> of solution.

It was impossible to obtain satisfactory calorimetric results for the rubidium and caesium salts of the hexahalogenorhenate(IV) anions, since these salts were too insoluble in the reaction mixture for the hydrolysis reaction to proceed to completion within an acceptable time. Results obtained for the oxidative hydrolysis of  $K_2[ReCl_6]$  and of  $K_2[ReBr_6]$  to tetraoxorhenate(VII) were much less satisfactory than those obtained for hydrolysis to rhenium dioxide; the former have therefore been discarded.

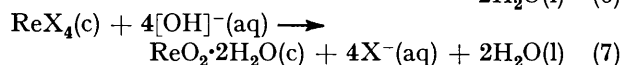
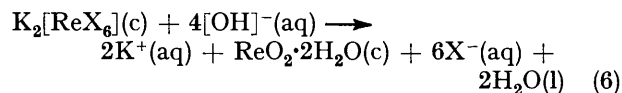
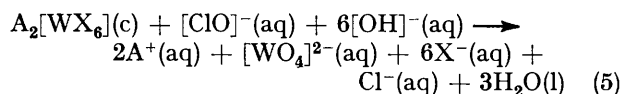
TABLE 1  
 Thermochemical results for hydrolyses

Compound	No. of samples	No. of hydrolyses	[NaOH] mol dm <sup>-3</sup>	Mean $\Delta H_{\text{hyd}}$	$\sigma^a$	$\Delta H_f$
					kJ mol <sup>-1</sup>	
K <sub>2</sub> [WCl <sub>6</sub> ]	2	6	0.86 <sup>b</sup>	-738	7	-1 380 <sup>c</sup>
K <sub>2</sub> [WBr <sub>6</sub> ]	3	9	0.86 <sup>b</sup>	-778 <sup>d</sup>	9	-1 066
Rb <sub>2</sub> [WBr <sub>6</sub> ]	3	9	0.86 <sup>b</sup>	-735 <sup>d</sup>	6	-1 107
Cs <sub>2</sub> [WBr <sub>6</sub> ]	3	9	0.86 <sup>b</sup>	-714 <sup>d</sup>	7	-1 142
K <sub>2</sub> [ReCl <sub>6</sub> ]	3	9	2	-264	5	-1 335 <sup>e</sup>
K <sub>2</sub> [ReBr <sub>6</sub> ]	2	16	2	-287	10	-1 038
$\beta$ -ReCl <sub>4</sub>	3	9	2	-400	15	-360
ReBr <sub>4</sub>	2	13	2	-275	17	-303

<sup>a</sup> Standard deviations, from which standard errors of the means and their confidence limits can be calculated by standard procedures (see, for example, E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7-9). <sup>b</sup> Containing 1.5% sodium hypochlorite. <sup>c</sup> *cf.*  $\Delta H_f(\text{K}_2\text{WCl}_6, \text{c}) = -1\,359\text{ kJ mol}^{-1}$  by bomb calorimetry (D. V. Korol'kov and G. N. Kudryashova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1759). <sup>d</sup> Corrected for reaction of the bromide ion released with hypochlorite, for which the standard enthalpy change is  $-32.6 \pm 0.4\text{ kJ mol}^{-1}$  (our measurements, *cf.*  $-33.1\text{ kJ mol}^{-1}$  quoted in J. P. King and J. W. Cobble, *J. Amer. Chem. Soc.*, 1960, **82**, 2111). <sup>e</sup> *cf.*  $\Delta H_f(\text{K}_2\text{ReCl}_6, \text{c}) = -1\,331\text{ kJ mol}^{-1}$  (R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609).

## RESULTS AND DISCUSSION

*Enthalpies of Formation.*—Our calorimetric results are summarised in Table 1. The hydrolyses studied proceeded quantitatively in alkaline or in alkaline hypochlorite solution, as shown in equations (5) for the hexahalogenotungstates(IV), (6) for the hexahalogenorhenates(IV), and (7) for the rhenium tetrahalides. The



enthalpy of formation,  $\Delta H_f^\ddagger$  of each compound was calculated from its measured enthalpy of hydrolysis and the appropriate ancillary thermochemical data (Table 2). For oxidative hydrolysis of hexabromo-salts, it is necessary to make allowance for the bromide-hypochlorite reaction (see footnote to Table 1).

The calorimetric results for ReCl<sub>4</sub> given in Table 1 were all obtained from samples prepared from the reaction of rhenium metal with SbCl<sub>5</sub>, using the frangible bulb apparatus. Results from these same samples obtained using the LKB calorimeter were more widely scattered, due to technical difficulties in handling this sensitive compound. These difficulties are associated with the filling and weighing of the fragile sample ampoules. Nonetheless the mean enthalpy of hydrolysis,  $-398\text{ kJ mol}^{-1}$ , agrees well with that reported in Table 1. Samples of ReCl<sub>4</sub> prepared from ReCl<sub>5</sub> and SbCl<sub>3</sub> were impossible to purify, completely, but their mean enthalpy of hydrolysis,  $-382\text{ kJ mol}^{-1}$  in  $2\text{ mol dm}^{-3}\text{ Na}[\text{OH}]$ , supports the Table 1 value.

Enthalpies of formation of chlorides and bromides of tungsten and of rhenium are listed in Table 3. The enthalpy of formation of ReCl<sub>4</sub> is close to that of ReCl<sub>5</sub>.

† It is not possible to obtain standard enthalpies of formation,  $\Delta H_f^\ominus$ , from our results. However, it seems likely that our  $\Delta H_f$  values are very close to  $\Delta H_f^\ominus$ , probably within our stated uncertainties.

This indicates that the stability of ReCl<sub>5</sub>(c) is marginal with respect to ReCl<sub>4</sub>(c). However, reasonable extrapolation of the available enthalpies of sublimation shows that ReCl<sub>5</sub>(g) is likely to be appreciably more stable than ReCl<sub>4</sub>(g). Our data are in accord with the

TABLE 2

Ancillary thermochemical data and sources used for the calculation of  $\Delta H_f$  (Table 1) from calorimetric measurements of hydrolysis, and for subsequent estimates of halide and electron affinities

Ion	$\Delta H_f/\text{kJ mol}^{-1}$	Ref.
[WO <sub>4</sub> ] <sup>2-</sup> (aq)	-1 073.2	a
[ReO <sub>4</sub> ] <sup>-</sup> (aq)	-791.6	c
Cl <sup>-</sup> (aq)	-167.1	b
Br <sup>-</sup> (aq)	-121.5	b
[ClO] <sup>-</sup> (aq)	-107.1	d
[OH] <sup>-</sup> (aq)	-230.0	b
K <sup>+</sup> (aq)	-252.2	b
Rb <sup>+</sup> (aq)	-251.1	b
Cs <sup>+</sup> (aq)	-258.0	b
H <sub>2</sub> O(l)	-285.8	b
ReO <sub>2</sub> ·2H <sub>2</sub> O(c)	-1 011.7	c

<sup>a</sup> H. C. Ko, T. Matsui, and L. G. Hepler, *Thermochim. Acta*, 1974, **10**, 211; I. Dellien, F. M. Hall, and L. G. Hepler, *Chem. Rev.*, 1976, **76**, 283. <sup>b</sup> *J. Chem. Thermodynamics*, 1975, **7**, 1; 1976, **8**, 603. <sup>c</sup> R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609. <sup>d</sup> J. E. McDonald, J. P. King, and J. W. Cobble, *J. Phys. Chem.*, 1960, **64**, 1345; J. D. Cox, J. B. Pedley, A. Kirk, S. Seilman, and L. G. Heath, CATCH Tables, Halogen Compounds, University of Sussex, 1972.

TABLE 3

Enthalpies of formation of (solid) chlorides and bromides of tungsten<sup>a</sup> and of rhenium

Compound	$\Delta H_f/\text{kJ mol}^{-1}$	Compound	$\Delta H_f/\text{kJ mol}^{-1}$
WCl <sub>2</sub>	-255	ReCl <sub>3</sub>	-264 <sup>b</sup>
WCl <sub>4</sub>	ca. -450	ReCl <sub>4</sub>	-361 <sup>c</sup>
WCl <sub>5</sub>	-510	ReCl <sub>5</sub>	-372 <sup>d</sup>
WCl <sub>6</sub>	-594		
		ReBr <sub>3</sub>	-167 <sup>b</sup>
WBr <sub>4</sub>	-146 <sup>e</sup>	ReBr <sub>4</sub>	-303 <sup>c</sup>
	or -300		
WBr <sub>5</sub>	-315		
WBr <sub>6</sub>	-348		

<sup>a</sup> Values for tungsten compounds taken from I. Dellien, F. M. Hall, and L. G. Hepler, *Chem. Rev.*, 1976, **76**, 283. <sup>b</sup> J. P. King and J. W. Cobble, *J. Amer. Chem. Soc.*, 1950, **82**, 2111; NBS Technical Note 270/4, 1969. <sup>c</sup> This work. <sup>d</sup> J. Burgess, C. J. W. Fraser, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1973, 501. <sup>e</sup> This value was reported in NBS Circular 500, 1952, but has been omitted from later compilations (*cf.* text).

known properties of these two chlorides, especially since  $\text{ReCl}_5$  is prepared in the presence of an excess of chlorine. It is possible to hazard a guess at the enthalpy of formation of  $\text{ReCl}_6$  (see above) from the values given in Table 3. We shall use an estimated value of  $-350 \text{ kJ mol}^{-1}$  for  $\Delta H_f(\text{ReCl}_6, c)$  later in this paper.

ations of thermodynamic data. Comparison with data for tetrabromides and tetrachlorides of other transition elements (Table 4) suggests that  $\Delta H_f(\text{WBr}_4, c)$  may be *ca.*  $-300 \text{ kJ mol}^{-1}$ . We shall use the latter estimate.

Average bond-dissociation energies of transition-metal tetrachlorides are collected in Table 5, which shows the

TABLE 4  
Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) of tetrachlorides and of tetrabromides of *d*- and *f*-block elements (in their standard states)

Tetrachlorides											
$\text{TiCl}_4$	-804 <sup>a</sup>	$\text{VCl}_4$	-569 <sup>a</sup>	$\text{CrCl}_4$	-102 <sup>b</sup>			$\text{RuCl}_4$	-52 <sup>b</sup>	$\text{PtCl}_4$	-326 <sup>b</sup>
$\text{ZrCl}_4$	-981 <sup>a</sup>	$\text{NbCl}_4$	-695 <sup>a</sup>	$\text{MoCl}_4$	-480 <sup>c</sup>			$\text{OsCl}_4$	-255 <sup>b</sup>		
$\text{HfCl}_4$	-990 <sup>a</sup>	$\text{TaCl}_4$	-702 <sup>a</sup>	$\text{WCl}_4$	<i>ca.</i> -450 <sup>c</sup>	$\text{ReCl}_4$	-361 <sup>d</sup>				
$\text{ThCl}_4$	-1 192 <sup>e</sup>	$\text{PaCl}_4$	-1 045 <sup>f</sup>	$\text{UCl}_4$	-1 019 <sup>g</sup>	$\text{NpCl}_4$	-992 <sup>e</sup>				
Tetrabromides											
$\text{TiBr}_4$	-617 <sup>a</sup>	$\text{VBr}_4$	-337 <sup>a</sup>								
$\text{ZrBr}_4$	-761 <sup>a</sup>			$\text{MoBr}_4$	-295 <sup>c</sup>						
				$\text{WBr}_4$	-300 <sup>h</sup>	$\text{ReBr}_4$	-303 <sup>d</sup>			$\text{PtBr}_4$	-159 <sup>b</sup>
$\text{ThBr}_4$	-950 <sup>e</sup>			$\text{UBr}_4$	-823 <sup>e</sup>	$\text{NpBr}_4$	-502 <sup>e</sup>				

<sup>a</sup> NBS Technical Note 270/5, 1971. <sup>b</sup> NBS Technical Note 270/4, 1969. <sup>c</sup> I. Dellen, F. M. Hall, and L. G. Hepler, *Chem. Rev.*, 1976, **76**, 283. <sup>d</sup> This work. <sup>e</sup> NBS Circular 500, 1952. <sup>f</sup> D. Brown, personal communication. <sup>g</sup> E. H. P. Cordfunke, W. Ouweltjes, and G. Prins, *J. Chem. Thermodynamics*, 1976, **8**, 241. <sup>h</sup> Estimated value (see text).

TABLE 5

Mean bond-dissociation energies<sup>a</sup> ( $\text{kJ mol}^{-1}$ ) for tetrachlorides of transition elements (in the gas phase)<sup>b</sup>

$\text{TiCl}_4$	430	$\text{VCl}_4$	382	$\text{CrCl}_4$	338			$\text{RuCl}_4$	295		
$\text{ZrCl}_4$	491	$\text{NbCl}_4$	443	$\text{MoCl}_4$	380			$\text{OsCl}_4$	339	$\text{PtCl}_4$	277 <sup>d</sup>
$\text{HfCl}_4$	498	$\text{TaCl}_4$	457	$\text{WCl}_4$	410 <sup>c</sup>	$\text{ReCl}_4$	362 <sup>c,d</sup>				

<sup>a</sup> Mean bond-dissociation energies (b.d.e.) have been calculated from:  $\text{b.d.e.} = \frac{1}{4}[-\Delta H_f(\text{MCl}_4, g) + \Delta H_{\text{sub}}(\text{M}) + 2\Delta H_{\text{diss}}(\text{Cl}_2, g)]$ . <sup>b</sup> The required thermodynamic data have been taken from NBS Technical Notes 270/4, 1969, or 270/5, 1971, unless stated otherwise. <sup>c</sup> Enthalpies of formation determined in the present investigation. <sup>d</sup> Enthalpies of sublimation of 170 and 180  $\text{kJ mol}^{-1}$  have been estimated by interpolation for the tetrachlorides of rhenium and platinum.

TABLE 6

Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) of alkali-metal salts of transition-metal  $[\text{MCl}_6]^{2-}$  and  $[\text{MBr}_6]^{2-}$  anions

M =	$\text{K}_2[\text{MCl}_6]$	$\text{Rb}_2[\text{MCl}_6]$	$\text{Cs}_2[\text{MCl}_6]$	$\text{K}_2[\text{MBr}_6]$	$\text{Rb}_2[\text{MBr}_6]$	$\text{Cs}_2[\text{MBr}_6]$
Ti	-1 747 <sup>a</sup>	-1 767 <sup>a</sup>	-1 797 <sup>a</sup>	-1 493 <sup>a</sup>	-1 517 <sup>a</sup>	-1 553 <sup>a</sup>
Zr	-1 932 <sup>a</sup>		-1 992 <sup>a</sup>		-1 612 <sup>b</sup>	-1 641 <sup>b</sup>
Hf	-1 957 <sup>a</sup>					
Nb	-1 594 <sup>a</sup>	-1 619 <sup>a</sup>	-1 663 <sup>a</sup>			
Ta	-1 648 <sup>a</sup>	-1 669 <sup>a</sup>	-1 711 <sup>a</sup>			
	-1 707 <sup>c</sup>	-1 736 <sup>c</sup>	-1 774 <sup>c</sup>			
Mo	-1 469 <sup>d</sup>	-1 495 <sup>d</sup>	-1 527 <sup>d</sup>			
W	-1 359 <sup>e</sup>	-1 429 <sup>e</sup>	-1 446 <sup>e</sup>	-1 065 <sup>f</sup>	-1 106 <sup>f</sup>	-1 133 <sup>f</sup>
	-1 380 <sup>f</sup>					
Re	-1 335 <sup>f</sup>			-1 036 <sup>f</sup>		
	-1 331 <sup>g</sup>					
Os	-1 171 <sup>a</sup>					
Ir	-1 197 <sup>a</sup>					
Pd	-1 187 <sup>a</sup>					
Pt				-1 040 <sup>a</sup>		

<sup>a</sup> Ref. 15. <sup>b</sup> S. A. Shchukarev, D. V. Korol'kova, and I. V. Vasil'kova, *Russ. J. Inorg. Chem.*, 1964, **9**, 980. <sup>c</sup> V. M. Tsintsina and E. K. Smirnova, *Russ. J. Inorg. Chem.*, 1969, **14**, 1729; E. K. Smirnova and I. V. Vasil'kova, *ibid.*, 1967, **12**, 292. <sup>d</sup> A. I. Efimov and L. P. Belorukova, *Russ. J. Inorg. Chem.*, 1967, **12**, 792. <sup>e</sup> D. V. Korol'kova and G. M. Kudryashova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1759. <sup>f</sup> This work. <sup>g</sup> R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1977, **70**, 2609.

Rhenium tetrabromide has still not been fully characterised; our enthalpy value relates to the material of the correct composition prepared as described in the Experimental section. This value for  $\Delta H_f(\text{ReBr}_4, c)$  is more exothermic than expected by comparison with other data (Tables 3 and 4), but some of these are also subject to some uncertainty. The situation with respect to  $\text{WBr}_4$  is even less satisfactory. A value of  $-146 \text{ kJ mol}^{-1}$  for  $\Delta H_f(\text{WBr}_4, c)$  was given in NBS Circular 500, published in 1952, but does not appear in later compil-

ations of thermodynamic data. Comparison with data for tetrabromides and tetrachlorides of other transition elements (Table 4) suggests that  $\Delta H_f(\text{WBr}_4, c)$  may be *ca.*  $-300 \text{ kJ mol}^{-1}$ . We shall use the latter estimate.

Average bond-dissociation energies of transition-metal tetrachlorides are collected in Table 5, which shows the expected trends of values both along rows and down columns of the Periodic Table. Our determined enthalpies of formation of hexachloro- and hexabromo-tungstates(IV) and -rhenates(IV) are compared with data for other transition-metal  $\text{A}_2[\text{MX}_6]$  salts in Table 6. This Table shows how  $\Delta H_f(\text{A}_2\text{MX}_6)$  varies along rows and down columns of the Periodic Table, as well as the effects of changing  $\text{A}^+$  ( $\text{A} = \text{K}, \text{Rb}, \text{or Cs}$ ) and  $\text{X}^-$  ( $\text{X} = \text{Cl or Br}$ ). The agreement of our results with those from earlier workers for

the standard enthalpies of formation of  $K_2[WCl_6]$  and of  $K_2[ReCl_6]$  is also apparent from the appropriate entries in this Table.

**Lattice Energies.**—For the purposes of calculating the lattice energies required in this study we employ the recently developed direct minimisation of the Huggins and Mayer<sup>13</sup> potential by Jenkins and Pratt,<sup>14,15</sup> which has been tested for cyanides.<sup>16,17</sup> The method is described in full in ref. 15; its outline is presented briefly here.

We write the total lattice-potential energy,  $U_{POT}$ , as the sum of the electrostatic,  $U_{ELEC}$ , dipole-dipole dispersion,  $U_{dd}$ , dipole-quadrupole dispersion,  $U_{qd}$ , and

$$U_{POT} = U_{ELEC} + U_{dd} + U_{qd} - U_R \quad (8)$$

$$\left( \frac{\partial U_{POT}(A_2MX_6)}{\partial a} \right)_{a=a_0} = 0 \quad (9)$$

repulsion,  $U_R$ , terms [equation (8)]. Applying the condition [equation (9)];  $a_0$  is the equilibrium value of

TABLE 7  
Coefficients for the total lattice potential, equation (12)

Salt	$a_0/\text{\AA}$	$U_{POT}(A_2MX_6)/$ $\text{kJ mol}^{-1}$	
		$A_0$	$A_1$
$K_2[WCl_6]$	9.875	1 570	280
$Rb_2[WCl_6]$	10.00	1 561	266
$Cs_2[WCl_6]$	10.27	1 537	238
$K_2[ReCl_6]$	9.840	1 576	280
$Rb_2[WBr_6]$	10.50	1 503	262
$Cs_2[WBr_6]$	10.70	1 493	243
$K_2[ReBr_6]$	10.385	1 511	275

which is determined in the study, has a close parametric relationship with  $\rho$ .

The total lattice-potential energies of the salts considered in the present work approximate closely to the parametric form of equation (12) in the region of  $q_X$

$$U_{POT} = A_0 + A_1 q_X \quad (12)$$

values of chemical interest. Values of the coefficients  $A_0$  and  $A_1$  of equation (12) are listed in Table 7.

TABLE 8

Data for the estimation of halide-ion affinities of tetrahalides of tungsten and of rhenium (all values in  $\text{kJ mol}^{-1}$ )

	$K_2[WCl_6]$	$Rb_2[WCl_6]$	$Cs_2[WCl_6]$	$K_2[ReCl_6]$	$Rb_2[WBr_6]$	$Cs_2[WBr_6]$	$K_2[ReBr_6]$
$\Delta H_f^\circ(A^+, g)$	514.5 <sup>a</sup>	494.9 <sup>b</sup>	460.0 <sup>a</sup>	514.5 <sup>a</sup>	494.9 <sup>a</sup>	460.0 <sup>a</sup>	514.5 <sup>a</sup>
$\Delta H_f(A_2MX_6, c)$	-1 380 <sup>c</sup>	-1 429 <sup>d</sup>	-1 446 <sup>d</sup>	-1 333 <sup>c</sup>	-1 107 <sup>e</sup>	-1 142 <sup>e</sup>	-1 038 <sup>e</sup>
$\Delta H_f(MX_6^{2-}, g)$	$B_0$	-838	-858	-829	-785	-569	-555
	$B_1$	280	266	238	280	262	275
$\Delta H_f(MX_4)$	total	-1 012	-1 023	-977	-942	-703	-693
	(c)	-447 <sup>e</sup>	-447 <sup>e</sup>	-447 <sup>e</sup>	-360	ca. -300 <sup>f</sup>	ca. -300 <sup>f</sup>
$\Delta H_f(X^-, g)$	(g)	-341 <sup>e</sup>	-341 <sup>e</sup>	-341 <sup>e</sup>			
		-246 <sup>e</sup>	-246 <sup>e</sup>	-246 <sup>e</sup>	-246 <sup>e</sup>	-234 <sup>e</sup>	-234 <sup>e</sup>
$\Delta H_{2x}$	$C_0(c)$	101	81	110	69	20	45
	$C_1$	-5	-25	19			
		280	266	238	280	262	275

<sup>a</sup> Ref. 22. <sup>b</sup> NBS Circular 500, 1952. <sup>c</sup> This work, see Table 1. <sup>d</sup> D. V. Korol'kov and G. N. Kudryashova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1759. <sup>e</sup> CATCH Tables, University of Sussex, 1974. <sup>f</sup> Estimated value, see text.

the cell length  $a$ ], true for all crystal lattices, to equation (8) leads to (10), and thence to (11). In equation (11),

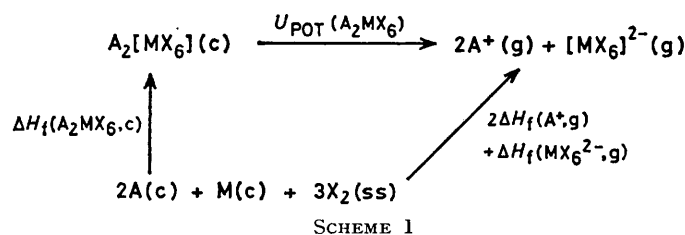
$$\left( \frac{\partial U_R}{\partial a} \right)_{a=a_0} = \left( \frac{\partial U_{ELEC}}{\partial a} \right)_{a=a_0} + \left( \frac{\partial U_{dd}}{\partial a} \right)_{a=a_0} + \left( \frac{\partial U_{qd}}{\partial a} \right)_{a=a_0} \quad (10)$$

$$\bar{r}(MX_6^{2-}) = \rho \ln \left[ \phi_0 + \left( \sum_{j=1}^3 \phi_j q_X^{(j-1)} \right)^{\frac{1}{\rho}} \right] \quad (11)$$

$q_X$  is the charge on the halogen atoms of the complex ion  $[MX_6]^{2-}$ ,  $\rho$  is the repulsion exponent,  $\phi_0$  to  $\phi_3$  are calculable,<sup>14</sup> and  $\bar{r}(MX_6^{2-})$  is the Huggins basic radius for the  $[MX_6]^{2-}$  anion. This radius is used within the Huggins and Mayer formalism to calculate the repulsion energy,  $U_R$ , and hence the total lattice potential energy,  $U_{POT}$ , via equation (8). In the present work, admitting a variable  $\rho$  parameter would introduce complications and in the absence of compressibility data make the evaluation of  $U_R$  difficult. The assumption that  $\rho$  is constant (taking the value to be 0.345  $\text{\AA}$ ) within the framework of the present method is made prior to the solution of equation (11), and hence errors introduced by such an assumption will be minimised since  $\bar{r}(MX_6^{2-})$ ,

We have also estimated lattice energies by approximate empirical methods, either by using repulsions in alkali-metal halides as a basis, or by interpolating appropriate values of  $r_0$  in the Born-Mayer equation from the A-M distance for  $q_X = 0$  to the A-X distance for  $q_X = -1$ . Such values are close to those derived from the direct-minimisation calculations detailed above.

**Halide-ion Affinities.**—In order to calculate halide-ion affinities for the tetrachlorides and tetrabromides of



tungsten and of rhenium [equations (2) and (3)] we require values for  $\Delta H_f(MX_6^{2-}, g)$ ,  $\Delta H_f(X^-, g)$ , and  $\Delta H_f(MX_4, g)$ . Equations (13) and (14) are generated from the Born-Fajans-Haber cycle (Scheme 1; ss = standard state) for salts with  $A = K, Rb, \text{ or } Cs$ . Equation (14)

$$U_{\text{POT}}(\text{A}_2\text{MX}_6) = 2\Delta H_f(\text{A}^+, \text{g}) + \Delta H_f(\text{MX}_6^{2-}, \text{g}) - \Delta H_f(\text{A}_2\text{MX}_6, \text{c}) \quad (13)$$

$$\Delta H_f(\text{MX}_6^{2-}, \text{g}) = U_{\text{POT}}(\text{A}_2\text{MX}_6) - 2\Delta H_f(\text{A}^+, \text{g}) + \Delta H_f(\text{A}_2\text{MX}_6, \text{c}) \quad (14)$$

$$\Delta H_f(\text{MX}_6^{2-}, \text{g}) = B_0 + B_1 q_x \quad (15)$$

can be expressed in the form of (15); values of coefficients  $B_0$  and  $B_1$  are given in Table 8. Equations (16) and (17) are now used to obtain halide-ion affinities\* for  $\text{MX}_4$ ; coefficients  $C_0$  and  $C_1$  [equation (17)] are also given in Table 8. We now need to know values of  $q_x$ , the

$$\Delta H_{2x} = \Delta H_f(\text{MX}_6^{2-}, \text{g}) - 2\Delta H_f(\text{X}^-, \text{g}) - \Delta H_f(\text{MX}_4) \quad (16)$$

$$\Delta H_{2x} = C_0 + C_1 q_x \quad (17)$$

effective charge on the halogen atoms, for each of our hexahalogenometallate(IV) complex anions. There is no self-consistent set of values for these. Kubo and Nakamura<sup>18</sup> estimated  $q_x$  values for a range of hexahalogenometallate(IV) anions from n.q.r. measurements. Subsequently Brown *et al.*<sup>19</sup> estimated  $q_x$  for a similar range of complexes, again from n.q.r. measurements, and obtained values 0.05 (or more) more negative than Kubo and Nakamura in the cases where data were available from both sources. Molecular-orbital (m.o.) calculations<sup>20</sup> tend to support the values of Brown *et al.* We therefore use their values of  $q_{\text{Cl}} = -0.62$  for  $[\text{WCl}_6]^{2-}$  and  $q_{\text{Cl}} = -0.56$  for  $[\text{ReCl}_6]^{2-}$ , and, on the basis of n.q.r. and m.o. evidence, estimate a value of  $q_{\text{Br}} = -0.55$  for  $[\text{WBr}_6]^{2-}$  and  $-0.50$  for  $[\text{ReBr}_6]^{2-}$ .

From Table 8 and  $q_{\text{Cl}} = -0.62$ ,<sup>19</sup> we find the values for the two-chloride ion affinity,  $\Delta H_{2\text{Cl}}$ , for  $\text{WCl}_4$  given in equations (18)–(20). The two-chloride ion affinity for  $\text{ReCl}_4$  is given by equation (21), using a value of  $q_{\text{Cl}} = -0.56$ .<sup>19</sup> The values for the two-bromide ion

$$\Delta H_{2\text{Cl}}(\text{WCl}_4, \text{c}) = 101 + 280q_{\text{Cl}} = -73 \text{ kJ mol}^{-1} (\text{K}^+ \text{ salt}) \quad (18)$$

$$\Delta H_{2\text{Cl}}(\text{WCl}_4, \text{c}) = 81 + 266q_{\text{Cl}} = -84 \text{ kJ mol}^{-1} (\text{Rb}^+ \text{ salt}) \quad (19)$$

$$\Delta H_{2\text{Cl}}(\text{WCl}_4, \text{c}) = 110 + 238q_{\text{Cl}} = -38 \text{ kJ mol}^{-1} (\text{Cs}^+ \text{ salt}) \quad (20)$$

$$\Delta H_{2\text{Cl}}(\text{ReCl}_4, \text{c}) = 68 + 280q_{\text{Cl}} = -89 \text{ kJ mol}^{-1} (\text{K}^+ \text{ salt}) \quad (21)$$

affinity for  $\text{WBr}_4$  depend strongly on the value taken for its standard enthalpy of formation. From our estimate of  $\Delta H_f(\text{WBr}_4, \text{c}) = -300 \text{ kJ mol}^{-1}$  (see above), we obtain the estimates for the two-bromide ion affinity shown in equations (22) and (23). In these equations

$$\Delta H_{2\text{Br}}(\text{WBr}_4, \text{c}) = 175 + 262q_{\text{Br}} = 31 \text{ kJ mol}^{-1} (\text{Rb}^+ \text{ salt}) \quad (22)$$

$$\Delta H_{2\text{Br}}(\text{WBr}_4, \text{c}) = 209 + 243q_{\text{Br}} = 75 \text{ kJ mol}^{-1} (\text{Cs}^+ \text{ salt}) \quad (23)$$

\* See footnote on p. 1143.

we use an estimated value (see above) of  $-0.55$  for  $q_{\text{Br}}$ . The two-bromide ion affinity of  $\text{ReBr}_4$  is given by equation (24), in which we use an estimate for  $q_{\text{Br}}$  of  $-0.50$  (see above).

$$\Delta H_{2\text{Br}}(\text{ReBr}_4, \text{c}) = 218 + 275q_{\text{Br}} = 81 \text{ kJ mol}^{-1} (\text{K}^+ \text{ salt}) \quad (24)$$

There are two unsatisfactory features in the above derivations of two-halide ion affinities. The first is the lack of a reliable value for the standard enthalpy of formation of  $\text{WBr}_4$ . For the present we feel that it is best to use our estimate of  $-300 \text{ kJ mol}^{-1}$ . The other thermochemical value which causes some concern is that for  $\Delta H_f^\ominus(\text{Cs}^+, \text{g})$ . There are two significantly different values published for this in standard thermochemical compilations.<sup>21,22</sup> Neither of these are quite as expected by extrapolation from the other alkali metals. Indeed, a value estimated from the trend for the other alkali metals would make our values for halide-ion affinities from caesium salts [equations (20) and (23)] closer to those from the analogous potassium and rubidium salts [equations (18), (19), and (22)]. We have accordingly chosen to give a lower weighting to the caesium-derived results in our final recommendations for two-halide ion affinities of these tetrahalides of tungsten and of rhenium (Table 9). It is impossible to give statistically

TABLE 9

Recommended (rounded) values for two-halide-ion affinities of tungsten and rhenium tetrahalides

Compound	$\Delta H_{2\text{Cl}}/$ kJ mol <sup>-1</sup>	Compound	$\Delta H_{2\text{Br}}/$ kJ mol <sup>-1</sup>
$\text{WCl}_4(\text{c})$	-70	$\text{WBr}_4(\text{c})$	50
$\text{ReCl}_4(\text{c})$	-90	$\text{ReBr}_4(\text{c})$	80

based uncertainty limits for these Table 9 values. Our subjective judgement suggests 90% confidence limits of the order of  $\pm 40 \text{ kJ mol}^{-1}$ , taking into account the difficulties mentioned in this paragraph and the uncertainties attendant on the choice of the values of  $q_x$  used in the assignment of the lattice energies. The two-chloride ion affinities of tungsten and rhenium tetrachlorides are compared with those for other tetrachlorides, both of *sp*- and of *d*-block elements, in Table 10.

*Electron Affinities.*—Two-electron affinities [equation (4);  $n = 2$ ] can be estimated for  $\text{WCl}_6$  and  $\text{WBr}_6$ , and also for  $\text{ReCl}_6$  if one assumes a reasonable value for the enthalpy of formation of this elusive compound. An appropriate thermochemical cycle is Scheme 2. From the relevant data given in Tables 8 and 11, the two-electron affinities shown in Table 11 have been calculated.

Despite the uncertainties in the estimates of electron affinity, it is clear that the magnitude of that for  $\text{WCl}_6$  is greater than that for  $\text{WBr}_6$ , and that the tentative value for  $\text{ReCl}_6$  is more negative than that for  $\text{WCl}_6$ . These two-electron affinities are less than those for two atoms of the respective halogens; the electron affinities for chlorine and bromine atoms in the gas phase are  $-696$  and  $-648 \text{ kJ}$  per two gram atoms respectively.<sup>23</sup>

TABLE 10  
Two-chloride-ion affinities ( $\text{kJ mol}^{-1}$ ) of tetrahalides <sup>a</sup>

GeCl <sub>4</sub> { (l) 43 (g) 7								
SnCl <sub>4</sub> { (l) -153 (g) -192			TcCl <sub>4</sub> { (c) -73 <sup>a</sup> (g) -153 <sup>a</sup>					
PbCl <sub>4</sub> { (l) -119 (g) -163								
TiCl <sub>4</sub> { (l) -36 (g) -76								
ZrCl <sub>4</sub> { (c) -54 (g) -164	NbCl <sub>4</sub> { (c) -78 (g) -171		MoCl <sub>4</sub> { (c) -73, -102 (g) -163, -192					
HfCl <sub>4</sub> { (c) -158 (g) -259	TaCl <sub>4</sub> { (c) -81 (g) -222		WCl <sub>4</sub> { (c) -70 <sup>b</sup> (g) -176 <sup>b</sup>		ReCl <sub>4</sub> { (c) -90 <sup>b</sup>	OsCl <sub>4</sub> { (c) -5 (g) -181		PtCl <sub>4</sub> { (c) -37

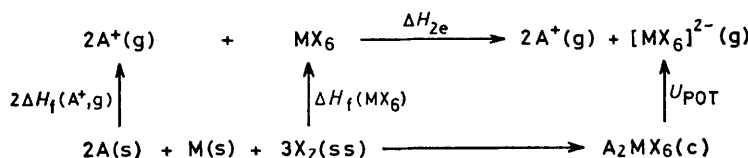
<sup>a</sup> Taken from ref. 15 unless where otherwise stated. <sup>b</sup> This work.

TABLE 11

Estimation of two-electron affinities,  $\Delta H_{2e}$  [equation (4);  $n = 2$ ] for hexahalides of tungsten and rhenium. All values are in  $\text{kJ mol}^{-1}$  and refer to 298 K

Salt	$U_{\text{POT}}(\text{A}_2\text{MX}_6, \text{c})$ <sup>a</sup>	$\Delta H_f(\text{MX}_6, \text{c})$	$\Delta H_{2e}(\text{MX}_6, \text{c})$	$\Delta H_f(\text{MX}_6, \text{g})$	$\Delta H_{2e}(\text{MX}_6, \text{g})$
K <sub>2</sub> [WCl <sub>6</sub> ]	1 396	-594	-411	-494	-511
Rb <sub>2</sub> [WCl <sub>6</sub> ]	1 396	-594	-422	-494	-522
Cs <sub>2</sub> [WCl <sub>6</sub> ]	1 389	-594	-376	-494	-461
Rb <sub>2</sub> [WBr <sub>6</sub> ]	1 359	-348	-383	-257 <sup>b</sup>	-474
Cs <sub>2</sub> [WBr <sub>6</sub> ]	1 359	-348	-348	-257 <sup>b</sup>	-439
K <sub>2</sub> [ReCl <sub>6</sub> ]	1 419	-350 <sup>c</sup>	-585	-255 <sup>d</sup>	-680

<sup>a</sup> Using the  $g_X$  values given in the text and  $A_0$  and  $A_1$  values from Table 7. <sup>b</sup> An estimated value of 91  $\text{kJ mol}^{-1}$  has been used for the enthalpy of sublimation of WBr<sub>6</sub>. <sup>c</sup> This is an extrapolated estimate for the enthalpy of formation of this elusive compound. <sup>d</sup> An estimated value of 95  $\text{kJ mol}^{-1}$  has been used for the enthalpy of sublimation of ReCl<sub>6</sub>.



SCHEME 2

Interestingly, the electron affinity for WF<sub>6</sub> (g) is -447  $\text{kJ mol}^{-1}$ ,<sup>24</sup> in comparison with an electron affinity of -333  $\text{kJ}$  per gram atom for fluorine (gas phase).<sup>23</sup>

*Single-ion Hydration Enthalpies.*—The calculation of lattice energies is also important in the estimation of single-ion hydration enthalpies from measurements of enthalpies of solution of appropriate salts. Recently, we estimated single-ion hydration enthalpies for the hexachloro- and hexabromo-rhenate(IV) anions from enthalpies of solution of the respective caesium<sup>25</sup> and potassium<sup>26</sup> salts. The simple Born-Mayer equation was used to calculate the lattice energies. We do not have sufficient data to apply the direct-minimisation approach to the determination of lattice energies of these caesium salts, but we cite above (Tables 7 and 10) values for K<sub>2</sub>[ReCl<sub>6</sub>]. Using this direct-minimisation lattice energy we derive a value of -740  $\text{kJ mol}^{-1}$  for the single-ion hydration energy of the hexachlororhenate(IV) anion; the Born-Mayer lattice energy leads to a value of -827  $\text{kJ mol}^{-1}$ . This difference arises from the differences obtained for the lattice energies from the two approaches.

We thank P. D. Robinson for some of the thermochemical results on K<sub>2</sub>[WCl<sub>6</sub>], Thorn Lighting Ltd. for helpful discussions and co-operation, and the S.R.C. both for a grant to purchase the LKB calorimeter and for the award of studentships (to S. J. C., I. H., K. F. P., and P. T.).

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