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LATTICE ENERGIES AND THERMOCHEMISTRY OF HEXAHALOMETALLATE(IV) COMPLEXES, A_2MX_6, WHICH POSSESS THE ANTIFLUORITE STRUCTURE

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I. Introduction

Salts having the general formula A_2MX_6 are formed by both transition and main-group elements (M) in the formal oxidation state (IV), where A is an alkali metal, thallium, or ammonium and X is a halogen. Accordingly, a study of such salts, in this chapter confined to those having the antifluorite (K_2PtCl_6) structure, generates interesting data embracing a wide section of the periodic table. This chapter concerns the role lattice energy plays in the thermochemistry of these salts.

Since this chapter went to press a similar study of the lattice energies of salts of general formula A_2MX_6 possessing noncubic structures has been made and will appear shortly (*40a*).

This study describes the attention that lattice energies of A_2MX_6 salts have received to date in the literature, reports some recent studies from this laboratory of the lattice energies of such salts as calculated using a new minimization procedure (*38, 39*), and, on the basis of these latter results, also presents estimates of the lattice energies of A_2MX_6 salts where M = Hf, Nb, Ta, Ru, and Sb to complete the study. All the salts considered (with the exception of a handful for which we estimate the lattice energy from thermochemical data) for which we have carried out an accurate evaluation of the lattice energy possess the antifluorite (K_2PtCl_6) structure, having a unit cell length a_0 and an M—X bond distance d ($d = u.a_0$) as the only variants from structure to structure.

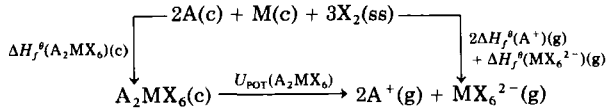
Lattice energies have been the subject of isolated studies (*16, 19, 22, 29, 36, 40, 51, 53, 68–70*) for isolated salts over the last decade and a half. Figure 1 represents the situation prior to the study that is the main subject of this article.

Figure 1 gives the salts, in periodic order, for which lattice energies had been reported prior to the commencement of this present study.

Table I gives the detailed results and references associated with Fig. 1 and indicates the type of calculation used to establish the lattice of the twenty-two A_2MX_6 salts considered.

A. Thermochemical Cycle

Incorporating the lattice energy into the Born–Fajans–Haber cycle:



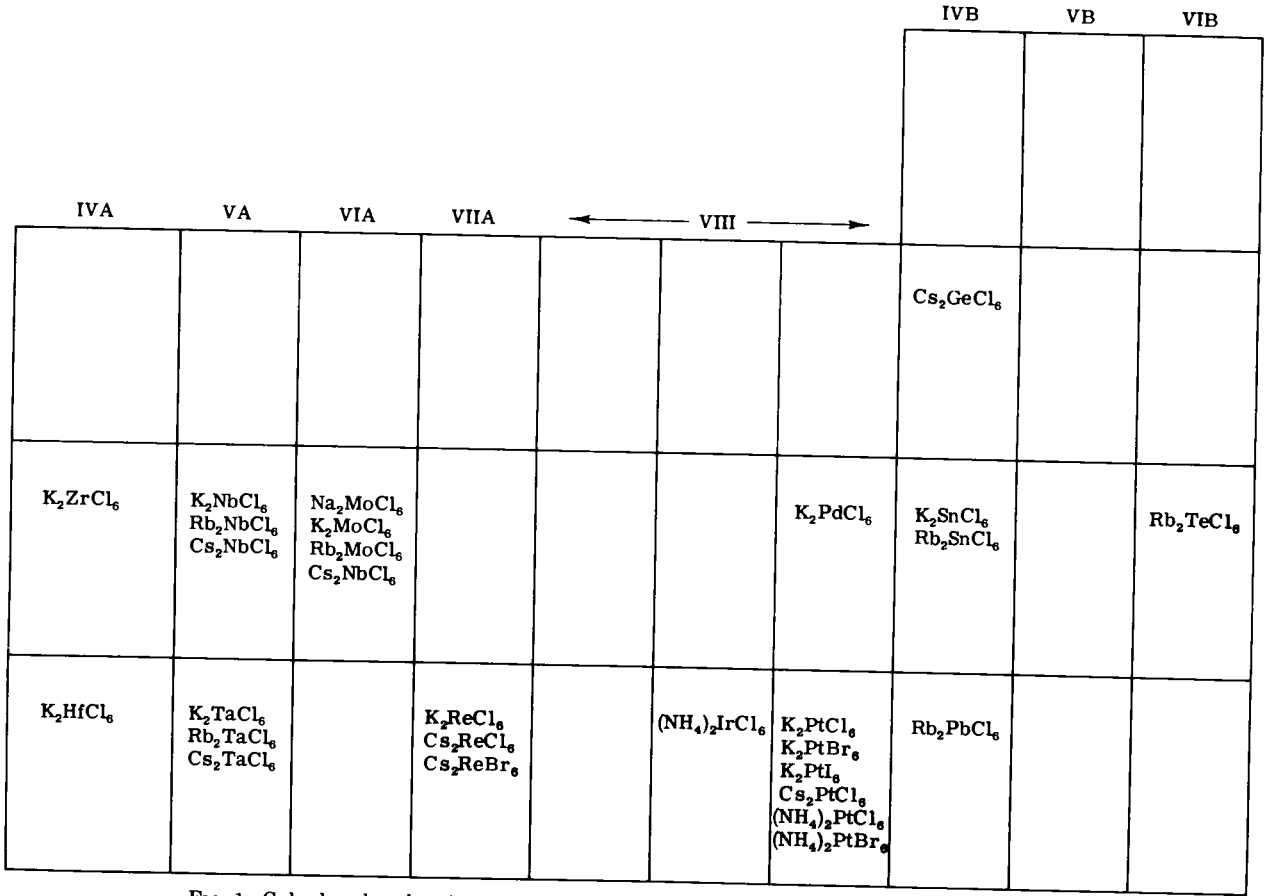


FIG. 1. Calculated and estimated lattice energies for A_2MX_6 salts: pre-1977.

TABLE I

LATTICE ENERGY CALCULATIONS FOR A_2MX_6 SALTS, PRE-1977. ENERGIES IN kJ mol^{-1}[a]

Complex Ion MX_6^{2-}	Counter Ion A^+	Webster and Collins (*69*) 1963 (j)	Efimov and Belorukova (*19*) 1967 (g)	Tsintsius and Smirnova (*68*) 1969 (g)	Hartley (29) 1972 (b)	Hartley (29) 1972 (c)	Lister (53) *et al.* 1974 (d)	Lister (53) *et al.* 1974 (e)	Lister (53) *et al.* 1974 (e)	Lister (53) *et al.* 1974 (f)	Lister (53) *et al.* 1974 (c)	Lister (53) *et al.* 1974 (g)	Welsh *et al.* (*70*) 1974 (j)	Lal and Westland (*51*) 1974 (c)	Gelbman and Westland (*22*) 1975 (a)	Jenkins and Smith (*40*) 1975 (k)	Burgess and Cartwright (*10a*) 1975 (b)	De Jonge (*16*) 1976 (e)	Jenkins (*36*) 1976 (h)	Makhija and Westland (*54a*) 1977 (c)
$ZrCl_6^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	(1571)	—	—	—	—	—
$ZrBr_6^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1501
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1464
$HfCl_6^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	(1574)	—	—	—	—	—
$HfBr_6^{2-}$	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1464
$NbCl_6^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	1586	—	—	—	—	—	—
	Rb^+	—	—	—	—	—	—	—	—	—	—	—	—	1569	—	—	—	—	—	—
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	1540	—	—	—	—	—	—
$TaCl_6^{2-}$	K^+	—	—	1582	—	—	—	—	—	—	—	—	—	1586	—	—	—	—	—	—
	Rb^+	—	—	1565	—	—	—	—	—	—	—	—	—	1569	—	—	—	—	—	—
	Cs^+	—	—	1540	—	—	—	—	—	—	—	—	—	1540	—	—	—	—	—	—
$MoCl_6^{2-}$	Na^+	—	1638	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	K^+	—	1602	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Rb^+	—	1567	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Cs^+	—	1537	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$ReCl_6^{2-}$	K^+	—	—	—	—	—	1448	1231	1170	1437	1555	1508	—	—	—	—	1506	—	—	—
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1453	—	—	—

$ReBr_6^{2-}$	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1399	—	—	—
$IrCl_6^{2-}$	NH_4^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1505	—	—	—
$PdCl_6^{2-}$	K^+	—	—	—	1519	1573	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$PtCl_6^{2-}$	K^+	—	—	—	1540	1598	1461	1327	1274	1450	1572	1521	—	—	—	—	1521	1323[b]	1468	—
	Cs^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1459	1337		—
	NH_4^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1507	—	—	—
$PtBr_6^{2-}$	K^+	—	—	—	1452	1506	1388	—	1301	1377	1498	1445	—	—	—	—	1451	1299	—	—
	NH_4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1439	—	—	—
PtI_6^{2-}	K^+	—	—	—	—	—	1264	—	—	—	1421	1317	—	—	—	—	—	—	—	—
$GeCl_6^{2-}$	Cs^+	—	—	—	—	—	—	—	—	—	—	—	1404	—	—	—	—	—	—	—
$SnCl_6^{2-}$	K^+	—	—	—	—	—	1425	—	—	1414	1533	1484	1370	—	(1586)	—	—	—	—	—
	Rb^+	1551	—	—	—	—	—	—	—	—	—	—	—	—	—	1259	—	—	—	—
$SnBr_6^{2-}$	K^+	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1505
$PbCl_6^{2-}$	Kb^+	—	—	—	—	—	—	—	—	—	—	—	1335	—	—	—	—	—	—	—
$TeCl_6^{2-}$	Rb^+	1578	—	—	—	—	—	—	—	—	—	—	—	—	—	1197	—	—	—	—

[a] Column heads: (a) Estimated from lattice energies calculated in reference 51 using relationships proposed in Gelbman and Westland (*22*). (b) Born–Mayer equation (*6*). (c) Kapustinskii equation (*46*). (d) Empirical. (e) Extended Born–Lande equation (*5*). (f) Simple Born–Lande equation (*5*). (g) Alternative Kapustinskii equation (*46*). (h) Direct minimization equation (*35*). (j) Wood's method (*2, 18, 21, 72, 73*). (k) Extended Huggins and Mayer equation (*33*).

[b] As corrected by DeJonge (*17*).

where (ss) indicates standard state (for A = NH_4 we must replace $U_{POT}(A_2MX_6)$ by $\{U_{POT}[(NH_4)_2MX_6] + 3RT\}$, the following equations are generated:

$$U_{POT}(A_2MX_6) = 2\Delta H_f^{\theta}(A^+)(g) + \Delta H_f^{\theta}(MX_6^{2-})(g) - \Delta H_f^{\theta}(A_2MX_6)(c) \quad (1)$$

for salts where A = K, Rb, Cs, Tl, and Ag, and

$$U_{POT}((NH_4)_2MX_6) = 2\Delta H_f^{\theta}(NH_4^+)(g) + \Delta H_f^{\theta}(MX_6^{2-})(g) - \Delta H_f^{\theta}((NH_4)_2MX_6)(c) - 3RT \quad (2)$$

for the ammonium salts.

We use these equations and the relationships:

$$\Delta H_f^{\theta}(MX_6^{2-})(g) = \Delta H_f^{\theta}(MX_6^{2-})(aq) - 2\Delta H_f^{\theta}(H^+)(g) - 2\Delta H_{hyd}^{\theta}(H^+)(g) - \Delta H_{hyd}^{\theta}(MX_6^{2-})(g) \quad (3)$$

$$\overline{\Delta H}_{X(ss)} = \Delta H_f^{\theta}(MX_6^{2-})(g) - 2\Delta H_f^{\theta}(X^-)(g) - \Delta H_f^{\theta}(MX_4)(ss) \quad (4)$$

to obtain enthalpies of hydration, $\Delta H_{hyd}^{\theta}(MX_6^{2-})(g)$, and enthalpies of formation, $\Delta H_f^{\theta}(MX_6^{2-})(g)$, for the gaseous ions as well as halide (X^-) ion affinities for MX_4 in the state (ss), where (ss) = (g), (l), or (c).

B. Bond Strength

We can define the metal–halogen bond strength in the MX_6^{2-} ion in two ways. First, with reference to the homolytic fission of the bond:

$$MX_6^{2-} \rightarrow M(g) + 6X(g) + 2\bar{e}$$

in which case the enthalpy change, $-\Delta H_f^a(MX_6^{2-})(g)$ of the reaction above can be employed as a measure of the average (homolytic) bond energy, $\overline{E(M-X)}_{hom}$, defined as:

$$\overline{E(M-X)}_{hom} = -\tfrac{1}{6}\Delta H_f^a(MX_6^{2-})(g) \quad (5)$$

Second, with reference to the heterolytic fission of the bond:

$$MX_6^{2-}(g) \rightarrow M^{4+}(g) + 6X^-(g)$$

we can define an average (heterolytic) bond energy, $\overline{E(M-X)_{het}}$, using the enthalpy change, $-\Delta H_f^i(MX_6^{2-})(g)$ of the reaction thus:

$$\overline{E(M-X)_{het}} = -\tfrac{1}{6}\Delta H_f^i(MX_6^{2-})(g) \qquad (6)$$

This latter bond energy has been referred to by Basolo and Pearson (*1*) as the coordinate bond energy and is recommended by them as the more informative for the study of ions of the type MX_6^{2-} on the grounds (i) that in common substitution reactions it is heterolytic, rather than homolytic fission, that occurs in the M–X bonds, (ii) that no process corresponding to:

$$MX_6^{2-}(g) \rightarrow M(g) + 6X(g) + 2\bar{e}$$

really exists, and (iii) that the ionic nature of the metal halogen bonds makes it natural to think of complexes dissociating into ions. However, at high temperature the homolytic fission occurs, and thus for consideration of reactions at high temperature and in certain redox reactions involving atom-transfer mechanisms, the former $\overline{E(M-X)_{hom}}$ definition may be more appropriate. Consequently we have chosen to cite both bond energies in what follows, although coordinate (heterolytic) bond energies, $\overline{E(M-X)_{het}}$, for the most part feature in our discussion.

The "total coordinate bond energy" (c.b.e.) defined by Pearson and Mawby (*58*) is defined as $6\overline{E(M-X)_{het}}$ = c.b.e. for MX_6^{2-} ions.

Figure 2 gives the energy diagram related to the above definitions.

C. Scope of Review

Figure 1 presented details of the calculations of the lattice energies of A_2MX_6 salts prior to the main studies reported here. Figure 3 shows the compounds that have received attention as a result of our *recent* minimization method in addition to values that have been estimated from these studies. Deriving from these lattice energies, using ancillary thermochemical data where available, we have computed halide ion affinities as defined in Eq. (4), and these have been obtained for the compounds $MX_4(ss)$ as indicated in Fig. 4.

The bond strengths of the metal–halogen bonds indicated in Fig. 5 have been obtained using the approach described in Section I,B above.

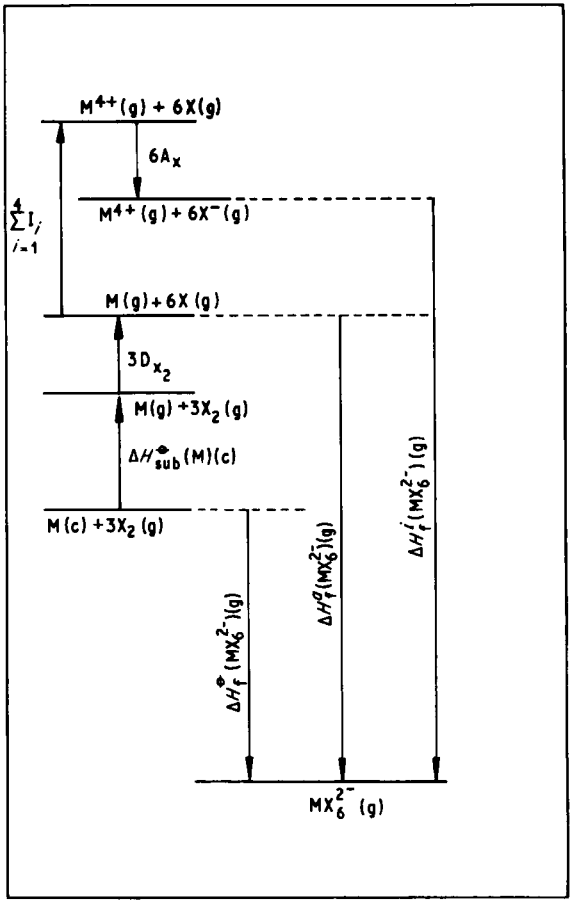


FIG. 2. Energy-thermodynamic correlation for bond-energy definitions.

We proceed now to a discussion of the method which is the main source of the lattice energies referred to in this chapter. The results are discussed in Section VIII and classified by ion type in periodic order in Section V. The lattice energies fall into three categories: (i) those derived from our new approach; (ii) those estimated on the basis of the results in (i); (iii) those obtained by other workers.

The study on the whole adds up to the generation of a systematic scheme for the examination of bond energies and other thermochemical properties across the periodic table to an extent not previously achieved.

IVA	VA	VIA	VIIA	VIII			IVB	VB	VIB
							K_2SiF_6 Rb_2SiF_6 Cs_2SiF_6 $(NH_4)_2SiF_6$		
K_2TiCl_6 K_2TiBr_6 Rb_2TiCl_6 Rb_2TiBr_6 Cs_2TiCl_6 Cs_2TiBr_6 $(NH_4)_2TiCl_6$		Cs_2CrF_6	K_2MnCl_6 Rb_2MnF_6 Rb_2MnCl_6 Cs_2MnF_6 Cs_2MnCl_6 $(NH_4)_2MnCl_6$		Rb_2CoF_6 Cs_2CoF_6	K_2NiF_6 Rb_2NiF_6	Cs_2GeCl_6		K_2SeBr_6 Rb_2SeCl_6 Cs_2SeCl_6 $(NH_4)_2SeCl_6$ $(NH_4)_2SeBr_6$
K_2ZrCl_6 Rb_2ZrCl_6 Cs_2ZrCl_6	K_2NbCl_6 Rb_2NbCl_6 Cs_2NbCl_6	Na_2MoCl_6 K_2MoCl_6 Rb_2MoCl_6 Cs_2MoCl_6	K_2TcCl_6 Rb_2TcCl_6	K_2RuCl_6		K_2PdCl_6 Rb_2PdCl_6 Cs_2PdCl_6 $(NH_4)_2PdCl_6$	K_2SnCl_6 Rb_2SnCl_6 Rb_2SnBr_6 Rb_2SnI_6 Cs_2SnCl_6 Cs_2SnBr_6 Cs_2SnI_6 $(NH_4)_2SnCl_6$ $(NH_4)_2SnBr_6$	Rb_2SbCl_6	K_2TeCl_6 Rb_2TeCl_6 Cs_2TeCl_6 Cs_2TeBr_6 Cs_2TeI_6 $(NH_4)_2TeCl_6$ $(NH_4)_2TeBr_6$
K_2HfCl_6	K_2TaCl_6 Rb_2TaCl_6 Cs_2TaCl_6	K_2WCl_6 K_2WBr_6 Rb_2WCl_6 Rb_2WBr_6 Cs_2WCl_6 Cs_2WBr_6	K_2ReCl_6 $K2ReBr_6$ Rb_2ReCl_6 Cs_2ReCl_6 $(NH_4)_2ReCl_6$	K_2OsCl_6 K_2OsBr_6 Cs_2OsCl_6 $(NH_4)_2OsCl_6$	$(NH_4)_2IrCl_6$	K_2PtCl_6 K_2PtBr_6 Rb_2PtCl_6 Cs_2PtCl_6 $(NH_4)_2PtCl_6$	Rb_2PbCl_6 Cs_2PbCl_6 $(NH_4)_2PbCl_6$		Cs_2PoBr_6 $(NH_4)_2PoCl_6$ $(NH_4)_2PoBr_6$

FIG. 3. Calculated and estimated lattice energies for A_2MX_6 salts: 1977.

IVA	VA	VIA	VIIA	VIII			IVB	VB	VIB
							SiF_4		
$TiCl_4$ $TiBr_4$						NiF_4	GeF_4 $GeCl_4$		
$ZrCl_4$	$NbCl_4$	$MoCl_4$				$PdCl_4$	$SnCl_4$		$TeCl_4$ $TeBr_4$
$HfCl_4$	$TaCl_4$	WCl_4 WBr_4	$ReCl_4$ $ReBr_4$	$OsCl_4$	$IrCl_4$	$PtCl_4$ $PtBr_4$	$PbCl_4$		

FIG. 4. Calculated halide ion affinities for MX_4 compounds.

IVA	VA	VIA	VIIA	← VIII →			IVB	VB	VIB
							Si-F		
Ti-Cl Ti-Br						Ni-F	Ge-F Ge-Cl		
Zr-Cl	Nb-Cl	Mo-Cl				Pd-Cl	Sn-Cl		Te-Cl Te-Br
Hf-Cl	Ta-Cl	W-Cl W-Br	Re-Cl Re-Br	Os-Cl	Ir-Cl	Pt-Cl Pt-Br	Pb-Cl		

FIG. 5. Calculated metal–halogen bond strengths.

II. Rigorous Lattice-Energy Calculation for A_2MX_6 Salts

A. THEORY

In the present study we have assigned a charge distribution (see Section II,B) in all cases to the MX_6^{2-} ion, based where possible on experimental data already available. Within a given ion MX_6^{2-} we have six atoms X bearing a charge q_X surrounding a central metal atom M bearing a charge q_M where:

$$q_M + 6q_X = -2 \tag{7}$$

The lattice potential energy of a salt A_2MX_6, $U_{POT}(A_2MX_6)$ is given by the sum of the electrostatic (U_{ELEC}), dipole–dipole dispersion (U_{dd}), dipole–quadrupole dispersion (U_{qd}), and repulsion (U_R) energies:

$$U_{POT}(A_2MX_6) = U_{ELEC} + U_{dd} + U_{qd} - U_R \tag{8}$$

and the condition that:

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

is used, and hence:

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

If, for a salt A_2MX_6, we regard it as consisting of two A^+ ions and an approximately spherical MX_6^{2-} complex ion, the approach of Huggins and Mayer (*33*) renders a parametric form for the repulsion energy:

$$\begin{aligned} U_R = {} & \frac{1}{2} bC_{++} \exp\left(\frac{2\bar{r}_{A^+}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions} \\ A_i^+}} \exp\left(\frac{-R_{A^+A_i^+}}{\rho}\right)\right] \\ & + bC_{+-} \exp\left(\frac{\bar{r}_{A^+} + \bar{r}_{MX_6^{2-}}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions} \\ MX_{6i}^{2-}}} \exp\left(\frac{-R_{A^+MX_{6i}^{2-}}}{\rho}\right)\right] \\ & + \frac{1}{2} bC_{--} \exp\left(\frac{2\bar{r}_{MX_6^{2-}}}{\rho}\right)\left[\sum_{\substack{\text{all ions} \\ MX_{6i}^{2-}}} \exp\left(\frac{-R_{MX_6^{2-}MX_{6i}^{2-}}}{\rho}\right)\right] \end{aligned} \tag{11}$$

applicable for this salt, where $C_{++} = 1.25$, $C_{+-} = 0.875$, and $C_{--} = 0.50$. All the distances involved in the summations are expressible as functions of a, the unit cell parameter, thus:

$$R_{ij} = a[(h + x_i - x_j)^2 + (k + y_i - y_j)^2 + (l + z_i - z_j)^2]^{1/2} = ak_{ij} \tag{12}$$

and hence U_R is differentiable and takes the form:

$$\begin{aligned} \left(\frac{\partial U_R}{\partial a}\right)_{a=a_0} = {} & -\frac{1}{2} bC_{++} \exp\left(\frac{2\bar{r}_{A^+}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions} \\ A_i^+}} \left(\frac{k_{A^+A_i^+}}{\rho}\right) \exp\left(\frac{-R_{A^+A_i^+}}{\rho}\right)\right] \\ & - bC_{+-} \exp\left(\frac{\bar{r}_{A^+} + \bar{r}_{MX_6^{2-}}}{\rho}\right)\left[2 \sum_{\substack{\text{all ions} \\ MX_{6i}^{2-}}} \left(\frac{k_{A^+MX_{6i}^{2-}}}{\rho}\right)\right. \\ & \left.\exp\left(\frac{-R_{A^+MX_{6i}^{2-}}}{\rho}\right)\right] \\ & -\frac{1}{2} bC_{--} \exp\left(\frac{2\bar{r}_{MX_6^{2-}}}{\rho}\right) \\ & \left[\sum_{\substack{\text{all ions} \\ MX_{6i}^{2-}}} \left(\frac{k_{MX_6^{2-}MX_{6i}^{2-}}}{\rho}\right) \exp\left(\frac{-R_{MX_6^{2-}MX_{6i}^{2-}}}{\rho}\right)\right] \end{aligned} \tag{13}$$

Herzig *et al.* (*32*) have expanded U_{ELEC}, the electrostatic energy for these salts, as a function of the cell length a, and an internal distance, d (corresponding to the M—X distance in the salt), and the charge distribution q_X on the terminal halogen atoms of the complex ion.

$$U_{ELEC} = K/a\left\{\alpha_0 + \left[\sum_{\substack{n=2\\ \text{even}}}^{x} \alpha_n (d/a)^n\right] q_X + \left[\sum_{\substack{n=2\\ \text{even}}}^{x} \beta_n (d/a)^n\right] {q_X}^2\right\} \tag{14}$$

whereupon

$$\left(\frac{\partial U_{ELEC}}{\partial a}\right)_{a=a_0} = \frac{K}{a_0}\left[\left(\frac{\partial M_{ELEC}}{\partial a}\right)_{a=a_0} - \frac{M_{ELEC}}{a_0}\right] \tag{15}$$

$$= -\frac{K}{{a_0}^2}\left[\alpha_0 + \sum_{\substack{n=2\\ \text{even}}}^{x} (n+1)\alpha_n \left(\frac{d}{a_0}\right)^n q_X + \sum_{\substack{n=2\\ \text{even}}}^{x} (n+1)\beta_n \left(\frac{d}{a_0}\right)^n {q_X}^2\right] \tag{16}$$

where M_{ELEC} is the electrostatic Madelung constant based on a_0. The derivatives $(\partial U_{dd}/\partial a)_{a=a_0}$ and $(\partial U_{qd}/\partial a)_{a=a_0}$ are evaluated using the polarizabilities of Pirenne and Kartheuser (*59*), treating the ions MX_6^{2-} as though they could be regarded as being comprised of six halide ions. The electron numbers were taken as 8, apart from the case where M = Tl, in which case the Herzfeld and Woolf formula (*31*) was employed. The summations necessary for the evaluation of the above derivatives took the form:

$$S_L^{A^+A^+} = 2\left[\sum_{\substack{\text{all ions}\\ A_i^+}}^{AA} (R_{A^+A_i^+})^{-L}\right] \tag{17}$$

$$S_L^{A^+X^-} = 2\left[\sum_{\substack{\text{all ions}\\ X_i^-}}^{AX} (R_{A^+X_i^-})^{-L}\right] \tag{18}$$

$$S_L^{X^-X^-} = 6\left[\sum_{\substack{\text{all ions}\\ X_i^-}}^{XX} (R_{X^-X_i^-})^{-L} - 4(R_{X^-X_{cis}^-})^{-L} - (R_{X^-X_{trans}^-})^{-L}\right] \tag{19}$$

where $R_{X^-X_{cis}^-}$ and $R_{X^-X_{trans}^-}$ are the halogen–halogen nearest and next-nearest neighbor distances in the same ion, MX_6^{2-}, and

$$U_{dd} = \tfrac{1}{2}[c_{++}{S_6}^{++} + c_{--}{S_6}^{--}] + c_{+-}{S_6}^{+-} \tag{20}$$

$$U_{qd} = \tfrac{1}{2}[d_{++}{S_8}^{++} + d_{--}{S_8}^{--}] + d_{+-}{S_8}^{+-} \tag{21}$$

where

$$c_{ij} = (2e^4 Q_i Q_j)/3(\epsilon_i + \epsilon_j) \tag{22}$$

$$d_{ij} = \tfrac{3}{2} c_{ij}[Q_i/p_i + Q_j/p_j] \tag{23}$$

$$Q_i = (3\alpha_i \epsilon_i)/2e^2 \tag{24}$$

α_i, ϵ_i, and p_i are the polarizability, characteristic energy, and electron number of the ion i and e is the electronic charge and, since

$$\left(\frac{\partial S_L{}^{ij}}{\partial a}\right)_{a=a_0} = -\sum_{\substack{\text{all}\\ j}} k_{ij} L R_{ij}^{-(L+1)} = \frac{-L S_L{}^{ij}}{a_0} \tag{25}$$

we have

$$\left(\frac{\partial U_{dd}}{\partial a}\right)_{a=a_0} = -\frac{6U_{dd}}{a_0} \tag{26}$$

and

$$\left(\frac{\partial U_{qd}}{\partial a}\right)_{a=a_0} = -\frac{8U_{qd}}{a_0} \tag{27}$$

Substitution of Eqs. (13), (16), (26), and (27) into Eq. (10) gives us an equation of the form:

$$\theta_1 \exp\left(\frac{2\bar{r}_{MX_6{}^{2-}}}{\rho}\right) + \theta_2 \exp\left(\frac{\bar{r}_{A^+} + \bar{r}_{MX_6{}^{2-}}}{\rho}\right) + \theta_3 \exp\left(\frac{2\bar{r}_{A^+}}{\rho}\right) = \theta_4 \tag{28}$$

where

$$\theta_1 = \left\{-\frac{1}{2} bC_{--} - \left[\sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \left(\frac{k_{MX_6{}^{2-}MX_{6i}^{2-}}}{\rho}\right) \exp\left(-\frac{R_{MX_6{}^{2-}MX_{6i}^{2-}}}{\rho}\right)\right]\right\} \tag{29}$$

$$\theta_2 = \left[-2bC_{+-} \sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \left(\frac{k_{A^+MX_{6i}^{2-}}}{\rho}\right) \exp\left(-\frac{R_{A^+MX_{6i}^{2-}}}{\rho}\right)\right] \tag{30}$$

$$\theta_3 = \left[-bC_{++} \sum_{\substack{\text{all ions}\\ A_i^+}} \left(\frac{k_{A^+A_i^+}}{\rho}\right) \exp\left(-\frac{R_{A^+A_i^+}}{\rho}\right)\right] \tag{31}$$

$$\theta_4 = \left[\frac{1}{a_0}\left(U_{ELEC} + 6U_{dd} + 8U_{qd} - K\left(\frac{\partial M_{ELEC}}{\partial a}\right)_{a=a_0}\right)\right] \tag{32}$$

In a particular salt, A_2MX_6, since we *know* the "basic" radius for the cation, A^+, $\bar{r}_{A^+}$ (A = K, Rb, Cs, Tl, NH_4), Eq. (28) becomes

$$\theta_1 \exp(2\bar{r}_{MX_6^{2-}}/\rho) + \eta_2 \exp(\bar{r}_{MX_6^{2-}}/\rho) + \eta_3 = 0 \tag{33}$$

where

$$\eta_2 = [\theta_2 \exp(\bar{r}_{A^+}/\rho)] \tag{34}$$

$$\eta_3 = [\theta_3 \exp(2\bar{r}_{A^+}/\rho) - \theta_4] \tag{35}$$

and hence we can solve Eq. (33) for $\bar{r}_{MX_6^{2-}}$:

$$\exp\left(\frac{\bar{r}_{MX_6^{2-}}}{\rho}\right) = \left[\frac{-\eta_2 \pm (\eta_2^2 - 4\theta_1\eta_3)^{1/2}}{2\theta_1}\right] \tag{36}$$

for a range of charge distributions on the MX_6^{2-} ion as represented by q_X, θ_4 being itself a function of q_X by virtue of Eq. (21).

$$\theta_4 = \sum_{i=0}^{2} A_i q_X^{\,i} \tag{37}$$

and hence

$$\bar{r}_{MX_6^{2-}} = \rho \ln\left[\phi_0 + \left(\sum_{j=1}^{3} \phi_j q_X^{(j-1)}\right)^{1/2}\right] \tag{38}$$

where

$$\phi_3 = 4\theta_1 A_2 \tag{39}$$

$$\phi_2 = 4\theta_1 A_1 \tag{40}$$

$$\phi_1 = \eta_2^{\,2} - 4\theta_1\theta_3[\exp(2\bar{r}_{A^+}/\rho) - A_0] \tag{41}$$

and

$$\phi_0 = (-\eta_2/2\theta_1) \tag{42}$$

In the present work, admitting a variable ρ parameter would introduce complications and, in the absence of compressibility data, makes the calculation of U_R difficult. Assumption that ρ is constant (taking the value to be 0.345 Å) within the framework of the present method is made prior to the solution of Eq. (38) and hence errors introduced by such an assumption will be minimized since $\bar{r}_{MX_6^{2-}}$, which is determined in the study, has a close parametric relationship with ρ. From

Eq. (38), it will be seen that

$$\exp\left(\frac{\bar{r}_{MX_6^{2-}}}{\rho}\right) = \left[\phi_0 + \left(\sum_{j=1}^{3} \phi_j q_X^{(j-1)}\right)^{1/2}\right] \tag{43}$$

and hence in Eq. (11), the charge dependence can be expressed as

$$U_R = U_R^{++} + U_R^{+-} + U_R^{--} \tag{44}$$

$$= U_R^{++} + \delta_0\left[\phi_0 + \left(\sum_{j=1}^{3} \phi_j q_X^{(j-1)}\right)^{1/2}\right] + \delta_1\left[\phi_0 + \left(\sum_{j=1}^{3} \phi_j q_X^{(j-1)}\right)^{1/2}\right]^2 \tag{45}$$

where

$$\delta_0 = 2bC_{+-}\exp\left(\frac{\bar{r}_{A^+}}{\rho}\right)\sum_{\substack{\text{all ions}\\ MX_{6i}^{2-}}} \exp\left(-\frac{R_{A^+MX_{6i}^{2-}}}{\rho}\right) = \left[U_R^{+-}\Big/\exp\left(\frac{\bar{r}_{MX_6^{2-}}}{\rho}\right)\right] \tag{46}$$

and

$$\delta_1 = \frac{1}{2}bC_{--}\sum_{\substack{\text{all ions}\\ MX_6^{2-}}} \exp\left(-\frac{R_{MX_6^{2-}MX_{6i}^{2-}}}{\rho}\right) = \left[U_R^{--}\Big/\exp\left(\frac{2\bar{r}_{MX_6^{2-}}}{\rho}\right)\right] \tag{47}$$

and hence

$$U_R = [U_R^{++} + \delta_0\phi_0 + \delta_1\phi_0^2 + \delta_1\phi_1] + [\delta_1\phi_2]q_X + [\delta_1\phi_3]q_X^2 + [\delta_0 + 2\phi_0\delta_1](\phi_1 + \phi_2 q_X + \phi_3 q_X^2)^{1/2} \tag{48}$$

U_{dd} and U_{qd} are charge independent, and U_{ELEC} can be written:

$$U_{ELEC} = \sum_{k=0}^{2} \gamma_k q_X^k \tag{49}$$

Hence the charge dependence of U_{POT}, as defined by Eq. (8) is given by

$$U_{POT} = \sum_{k=0}^{2} \gamma_k q_X^k - [U_R^{++} + \delta_0\phi_0 + \delta_1\phi_0^2 + \delta_1\phi_1] - \delta_1\phi_2 q_X - \delta_1\phi_3 q_X^2 - (\delta_0 + 2\phi_0\delta_1)(\phi_1 + \phi_2 q_X + \phi_3 q_X^2)^{1/2} + U_{dd} + U_{gd} \tag{50}$$

$$U_{POT} = [\gamma_0 - U_R^{++} + U_{dd} + U_{qd} - \delta_0\phi_0 - \delta_1\phi_0^2 - \delta_1\phi_1] + q_X[\gamma_1 - \delta_1\phi_2] + q_X^2[\gamma_2 - \delta_1\phi_3] - (\delta_0 + 2\phi_0\delta_1)(\phi_1 + \phi_2 q_X + \phi_3 q_X^2)^{1/2} \tag{51}$$

TABLE II

CHARGE DISTRIBUTIONS ON MX_6^{2-} IONS FROM LITERATURE SOURCES[a]

Group	Ion MX_6^{2-}	Calculated q_X: Jørgensen (42–45)	Calculated q_X: Jørgensen with Madelung correction (42–45)	Calculated q_X: Average	Experimental q_X: Cotton and Harris (12)	Experimental q_X: Kubo and Nakamura (50)	Experimental q_X: Brown *et al.* (9)	Adopted value q_X
IVA	$TiCl_6^{2-}$	−0.44	−0.79	−0.61	—	—	—	−0.61
	$TiBr_6^{2-}$	−0.44	−0.74	−0.59	—	—	—	−0.59
	$ZrCl_6^{2-}$	−0.42	−0.91	−0.66	—	—	—	−0.66
	$HfCl_6^{2-}$	—	—	—	—	—	—	(−0.66)[b]
VA	$NbCl_6^{2-}$	−0.40	−0.89[d]	−0.65	—	—	—	−0.65
	$TaCl_6^{2-}$	—	—	—	—	—	—	(−0.65)[b]
VIA	CrF_6^{2-}	−0.42	−0.88	−0.65	—	—	—	−0.65
	$MoCl_6^{2-}$	−0.40	−0.81	−0.60	—	—	—	−0.60
	WCl_6^{2-}	—	—	—	—	−0.43	−0.62	−0.62
	WBr_6^{2-}	—	—	—	—	—	—	(−0.55)[b]
VIIA	MnF_6^{2-}	−0.40	−0.86	−0.63	—	—	—	−0.63
	$MnCl_6^{2-}$	−0.40	−0.71	−0.55	—	—	—	−0.55
	$ToCl_6^{2-}$	−0.35	−0.64	−0.49	—	—	—	−0.49
	$ReCl_6^{2-}$	—	—	—	−0.55	−0.45	−0.56	−0.56
	$ReBr_6^{2-}$	—	—	—	—	−0.39	—	(−0.5)[c]
VIII	$OsCl_6^{2-}$	—	—	—	−0.53	−0.47	−0.51	−0.51
	$OsBr_6^{2-}$	—	—	—	—	—	—	(−0.45)[b]
	CoF_6^{2-}	−0.40	−0.79	−0.59	—	—	—	−0.59
	$IrCl_6^{2-}$	—	—	—	−0.48	−0.47	−0.47	−0.47
	NiF_6^{2-}	−0.40	−0.75	−0.57	—	—	—	−0.57
	$PdCl_6^{2-}$	−0.36	−0.63	−0.49	—	−0.43	—	−0.43
	$PdBr_6^{2-}$	−0.35	−0.60[d]	−0.48	—	−0.37	—	−0.37
	$PtCl_6^{2-}$	−0.34	−0.68	−0.51	−0.45	−0.44	−0.45	−0.44[d]
	$PtBr_6^{2-}$	−0.33	−0.63	−0.48	—	−0.38	—	−0.38
IVB	SiF_6^{2-}	−0.36	−1.33	−0.84	—	—	—	−0.84
	GeF_6^{2-}	−0.36	−1.21	−0.78	—	—	—	−0.78
	$GeCl_6^{2-}$	−0.35	−1.10	−0.73	—	—	—	−0.73
	$SnCl_6^{2-}$	−0.36	−1.01	−0.74	—	−0.66	—	−0.66
	$SnBr_6^{2-}$	−0.35	−0.90	−0.63	—	−0.60	—	−0.60
	SnI_6^{2-}	−0.33	−0.80	−0.56	—	−0.55	—	−0.55
	$PbCl_6^{2-}$	—	—	—	—	−0.63	—	−0.63
VIB	$SeCl_6^{2-}$	−0.31	−0.60	−0.45	—	−0.56	—	−0.56
	$SeBr_6^{2-}$	−0.30	−0.55	−0.42	—	−0.47	—	−0.47
	$TeCl_6^{2-}$	−0.32	−0.69	−0.50	—	−0.68	—	−0.68
	$TeBr_6^{2-}$	−0.30	−0.64	−0.47	—	−0.58	—	−0.58
	TeI_6^{2-}	−0.29	−0.53	−0.41	—	−0.48	—	−0.48
	$PoCl_6^{2-}$	—	—	—	—	—	—	(−0.7)[b]
	$PoBr_6^{2-}$	—	—	—	—	—	—	(−0.6)[b]

[a] Values adopted in the current work are given in the right-hand column of the table.

[b] Estimated

[c] Kubo and Nakamura (*50*) disagree with the adopted value for $ReCl_6^{2-}$, and so this value is estimated.

[d] As used in reference (*38a*).

[e] $d = u \cdot a_0$ has been estimated in the absence of data for the purposes of using Jørgensen's approach to calculate q_X.

B. Charge Distribution in MX_6^{2-} Ions

Ideally with precise crystal structures and precise calculations, from plots of $\bar{r}_{MX_6^{2-}}$ against the charge q_X on the terminal halogen atom we ought to be able to determine q_X uniquely for a given ion. However, as in our previous work, in order to obtain a reliable discriminant for such a determination we really require to include in a study such as this, salts that exhibit at least two differing crystal structures within the series of different cations studied. This inclusion will be made later, (*40a*) but the present work is limited in that it includes only salts with the antifluorite structure, and consequently no estimate of the charge distribution in the complex ions can be gained from the plots of $\bar{r}_{MX_6^{2-}}$ versus q_X. Accordingly we have to resort to other studies to estimate the value of q_X for a given ion, uncertain though such estimates may be.

Jørgensen *et al.* (*42–45*) have detailed a method for the estimation of ionicities in complex ions MX_6^{2-}, both with and without a Madelung correction, using differential ionization energies as a measure of the electronegativities of the atoms involved. They claim that the calculations having the correction give the better results, but, as Table II indicates, this does not appear to be borne out when the Jørgensen charges (which we calculated using his method) are compared to the experimental estimates of Kubo and Nakamura (*50*) or Brown *et al.* (*9*). In fact an average of the two Jørgensen charges seems more appropriate, and we have chosen such an average when no experimental determination of q_X was available. The right-hand column of Table II, which lists the various determinations, gives the value of q_X we have used in this study. Having selected q_X for an ion in question, we determine from Eq. (38) a radius $\bar{r}_{MX_6^{2-}}$ for each salt A_2MX_6, which should be (and usually is found to be) practically constant for a given ion. We can calculate U_R corresponding to this "basic" radius $\bar{r}_{MX_6^{2-}}$ for the complex ion and hence determine the total lattice potential energy $U_{POT}(A_2MX_6)$ for each salt.

III. Estimated Lattice Energies

The vast majority of lattice energies cited in this chapter have been rigorously evaluated; however, a few are estimated in three different ways. The first takes known $\Delta H_f^\theta(A_2MX_6)(c)$ data for the salt A_2MX_6 (for which no lattice energy has been calculated) in conjunction with $\Delta H_f^\theta(MX_6^{2-})(g)$ data derived from salts for which the lattice potential energy and enthalpy of formation are known, to give an estimate of $U_{POT}(A_2MX_6)$. The results for these lattice energies are quoted in parentheses in Table III. The second method of estimation takes into

TABLE III

SUMMARY TABLE OF LATTICE ENERGY VALUES FOR A_2MX_6 SALTS AS CALCULATED BY THE NEW MINIMIZATION APPROACH DEVELOPED IN THIS CHAPTER AND JENKINS AND PRATT (*39*)

		Å		Adopted	kJ mol^{-1}					Å
MX_6^{2-}	A^+	a_0	d	q_X	U_{ELEC}	U_{dd}	U_{qd}	U_R	U_{POT}	$\bar{r}_{MX_6^{2-}}$
$TiCl_6^{2-}$	K^+	9.792	2.35	−0.61	1370	116	10	84	1412	2.48
	Rb^+	9.922	2.33	−0.61	1374	127	11	76	1415	2.47
	Cs^+	10.219	2.35	−0.61	1354	145	15	112	1402	2.50
	NH_4^+	9.89	2.37	−0.61	1356	140	13	96	1413	2.50
	(Tl^+)			−0.61					(1560)	
$TiBr_6^{2-}$	Rb^+	10.39	2.60	−0.59	1255	155	15	84	1341	2.62
	Cs^+	10.57	2.64	−0.59	1235	182	20	98	1339	2.61
	(K^+)			−0.59					(1379)	
$ZrCl_6^{2-}$	Rb^+	10.178	2.44	−0.66	1292	113	10	67	1348	2.45
	Cs^+	10.407	2.45	−0.66	1287	133	14	86	1348	2.49
$HfCl_6^{2-}$	Cs^+	10.42	2.60	−0.66	1225	141	15	66	1315	2.37
CrF_6^{2-}	Cs^+	9.02	1.73	−0.65	1656	92	10	155	1603	2.08
$MoCl_6^{2-}$	K^+	9.85	2.30	−0.60	1393	107	8	90	1418	2.54
	(Na^+)			−0.60					(1526)	
	(Rb^+)			−0.60					(1399)	
	(Cs^+)			−0.60					(1347)	
WCl_6^{2-}	K^+	9.875	2.36	−0.62	1358	110	9	79	1398	2.50
	Rb^+	10.00	2.36	−0.62	1354	122	11	90	1397	2.47
	Cs^+	10.27	2.36	−0.62	1343	141	15	107	1392	2.51
WBr_6^{2-}	Rb^+	10.50	2.48	−0.55	1321	130	11	101	1361	2.73
	Cs^+	10.70	2.48	−0.55	1310	152	16	116	1362	2.72
	(K^+)			−0.55					(1408)	
MnF_6^{2-}	Rb^+	8.43	1.69	−0.63	1752	87	8	159	1688	1.99
	Cs^+	8.92	1.74	−0.63	1670	99	11	160	1620	2.05
$MnCl_6^{2-}$	K^+	9.644	2.28	−0.55	1438	123	10	109	1462	2.51
	Rb^+	9.838	2.28	−0.55	1426	132	12	117	1451	2.50
	NH_4^+	9.82	2.24	−0.55	1440	136	13	126	1464	2.56
$TcCl_6^{2-}$	K^+	9.83	2.35	−0.49	1429	113	9	108	1443	2.59
$ReCl_6^{2-}$	K^+	9.84	2.35	−0.56	1386	111	9	90	1416	2.54
$ReBr_6^{2-}$	K^+	10.385	2.48	−0.5	1348	119	10	102	1375	2.81
$OsCl_6^{2-}$	K^+	9.729	2.36	−0.51	1419	124	10	106	1447	2.54
$OsBr_6^{2-}$	K^+	10.30	2.51	−0.45	1366	130	11	111	1396	2.80
CoF_6^{2-}	Rb^+	8.46	1.7	−0.59	1755	86	8	161	1688	2.00
	Cs^+	8.914	1.7	−0.59	1692	98	11	169	1632	2.07
$IrCl_6^{2-}$	NH_4^+	9.87	2.47	−0.47	1394	151	15	118	1442	2.56
NiF_6^{2-}	K^+	8.1088	1.78	−0.57	1774	84	7	144	1721	1.94
	Rb^+	8.462	1.71	−0.57	1757	86	8	163	1688	2.01
$PdCl_6^{2-}$	NH_4^+	9.84	2.30	−0.43	1470	138	13	140	1481	2.61
$PtCl_6^{2-}$	K^+	9.755	2.34	−0.44	1461	119	10	122	1468	2.60
	Rb^+	9.901	2.33	−0.44	1455	129	11	131	1464	2.56
	Cs^+	10.215	2.35	−0.44	1424	146	16	141	1444	2.58
	NH_4^+	9.858	2.37	−0.44	1446	142	13	134	1468	2.62
	Tl^+	9.779	2.30	−0.44	1473	247	27	201	1546	2.60
	(Ag^+)			−0.44					(1773)	
	(Ba^{2+})			−0.44					(2047)	

TABLE III (*Continued*)

MX_6^{2-}	A^+	Å		Adopted	kJ mol^{-1}					Å
		a_0	d	q	U_{ELEC}	U_{dd}	U_{qd}	U_R	U_{POT}	$\bar{r}_{MX_6^{2-}}$
$PtPr_6^{2-}$	K^+	10.293	2.46	−0.38	1414	125	11	127	1423	2.85
	(Ag^+)			−0.38					(1791)	
SiF_6^{2-}	K^+	8.133	1.75	−0.84	1676	81	6	93	1670	1.79
	Rb^+	8.452	1.69	−0.84	1688	86	8	113	1639	1.87
	Cs^+	8.919	1.69	−0.84	1639	98	11	144	1604	2.01
	Tl^+	8.568	1.71	−0.84	1665	173	20	183	1675	2.05
	NH_4^+	8.395	1.72	−0.84	1676	97	10	126	1657	1.94
	NH_4^+	8.395	1.69	−0.84	1694	96	9	134	1665	1.96
GeF_6^{2-}	Cs^+	9.021	1.80	−0.78	1598	93	11	129	1573	2.02
	NH_4^+	8.46	1.72	−0.78	1691	92	9	135	1657	1.99
$GeCl_6^{2-}$	Cs^+	10.21	2.35	−0.73	1305	146	16	92	1375	2.43
$SnCl_6^{2-}$	K^+	10.002	2.45	−0.66	1289	107	9	53	1352	2.41
	K^+	9.982	2.41	−0.66	1310	105	8	60	1363	2.45
	Rb^+	10.118	2.43	−0.66	1300	117	10	69	1358	2.43
	Rb^+	10.096	2.42	−0.66	1303	119	10	71	1361	2.43
	Cs^+	10.381	2.44	−0.66	1291	135	14	88	1352	2.48
	Cs^+	10.355	2.42	−0.66	1298	137	14	91	1358	2.48
	Tl^+	9.97	2.39	−0.66	1319	224	24	130	1437	2.55
	NH_4^+	10.060	2.41	−0.66	1307	126	11	75	1369	2.49
	NH_4^+	10.044	2.42	−0.66	1304	128	12	74	1370	2.48
$SnBr_6^{2-}$	Rb^+	10.64	2.61	−0.60	1244	128	11	74	1309	2.69
	Cs^+	10.81	2.65	−0.60	1224	154	16	88	1306	2.67
	NH_4^+	10.59	2.59	−0.60	1250	136	13	80	1319	2.74
SnI_6^{2-}	Rb^+	11.60	2.84	−0.55	1165	126	11	76	1226	3.11
	Cs^+	11.63	2.85	−0.55	1162	156	16	91	1243	3.03
$PbCl_6^{2-}$	Rb^+	10.197	2.49	−0.63	1283	115	10	65	1343	2.45
	Cs^+	10.415	2.50	−0.63	1278	136	14	84	1344	2.48
	NH_4^+	10.135	2.48	−0.63	1289	125	11	70	1355	2.50
$SeCl_6^{2-}$	Rb^+	9.978	2.39	−0.56	1369	127	11	98	1409	2.50
	Cs^+	10.266	2.41	−0.56	1350	145	15	113	1397	2.52
	NH_4^+	9.935	2.38	−0.56	1375	136	13	104	1420	2.55
$SeBr_6^{2-}$	K^+	10.363	2.54	−0.47	1345	127	11	104	1379	2.81
	NH_4^+	10.46	2.56	−0.47	1332	147	14	113	1380	2.81
$TeCl_6^{2-}$	Rb^+	10.233	2.51	−0.68	1249	113	10	51	1321	2.38
	Rb^+	10.233	2.53	−0.68	1239	115	10	48	1316	2.35
	Cs^+	10.447	2.51	−0.68	1249	132	13	71	1323	2.44
	Tl^+	10.107	2.48	−0.68	1264	211	22	105	1392	2.54
	NH_4^+	10.178	2.54	−0.68	1227	126	11	46	1318	2.37
	NH_4^+	10.20	2.53	−0.68	1237	122	11	50	1320	2.41
$TeBr_6^{2-}$	Cs^+	10.91	2.62	−0.58	1243	141	14	92	1306	2.73
	Cs^+	10.918	2.69	−0.58	1214	147	15	84	1292	2.70
	NH_4^+	10.728	2.68	−0.58	1222	132	12	72	1294	2.76
TeI_6^{2-}	Cs^+	11.721	2.91	−0.48	1175	152	15	96	1246	3.10
$PoCl_6^{2-}$	NH_4^+	10.35	2.38	−0.7	1300	100	8	70	1338	2.60
$PoBr_6^{2-}$	Cs^+	11.01	2.64	−0.6	1223	134	13	83	1286	2.74
	NH_4^+	10.84	2.60	−0.6	1242	114	10	74	1292	2.83

account the approximate equality of the lattice energies,

$$U_{POT}(K_2MX_6) \simeq U_{POT}((NH_4)_2MX_6) \tag{52}$$

and estimates the lattice energy of a potassium salt from that of an ammonium salt and vice versa; again they are quoted in parentheses in Table III. This subterfuge is resorted to only in cases where we stand to generate extra thermochemical data that could not otherwise be obtained. The third approach stems from the apparent rectilinear relationships (Figs. 6–9) between our calculated $U_{POT}(A_2MX_6)$ values and

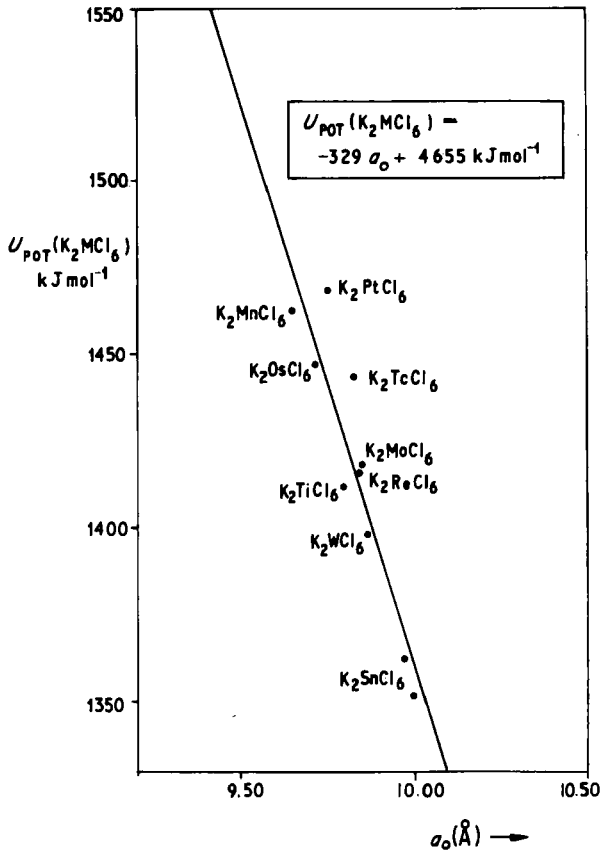


FIG. 6. Calculated lattice energy for potassium salts, K_2MCl_6, as a function of the cubic cell parameter, a_0. The relationship $U_{POT}(K_2MCl_6) = -329a_0 + 4655$ kJ mol^{-1} is found.

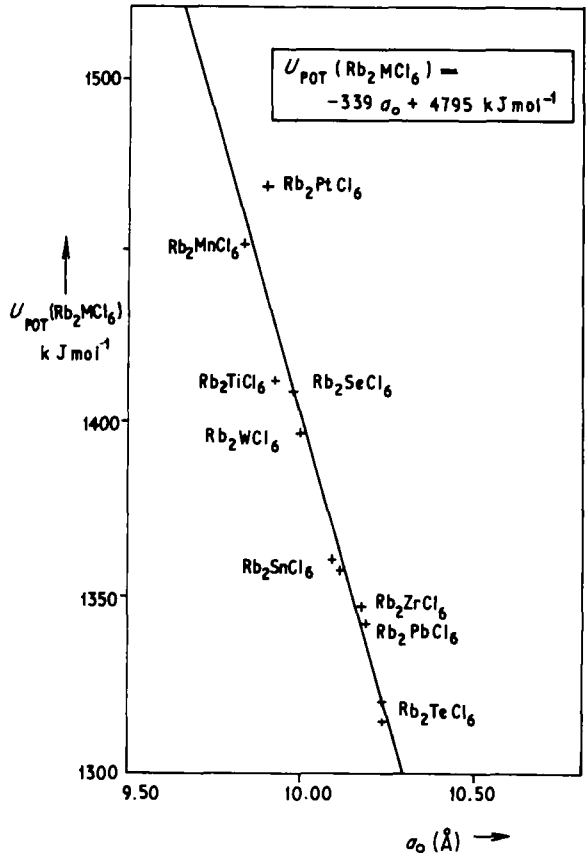


FIG. 7. Calculated lattice energy for rubidium salts, Rb_2MCl_6, as a function of the cubic cell parameter, a_0. The relationship $U_{POT}(Rb_2MCl_6) = -339a_0 + 4795$ kJ mol^{-1} is found.

the cell constant a_0 for a particular cation A, for which the following parametric relationships (least-square fits) are obtained:

$$U_{POT}(K_2MCl_6) = -329a_0 + 4655 \text{ kJ mol}^{-1} \quad (53)$$

$$U_{POT}(Rb_2MCl_6) = -339a_0 + 4795 \text{ kJ mol}^{-1} \quad (54)$$

$$U_{POT}(Cs_2MCl_6) = -348a_0 + 4969 \text{ kJ mol}^{-1} \quad (55)$$

$$U_{POT}((NH_4)_2MCl_6) = -309a_0 + 4486 \text{ kJ mol}^{-1} \quad (56)$$

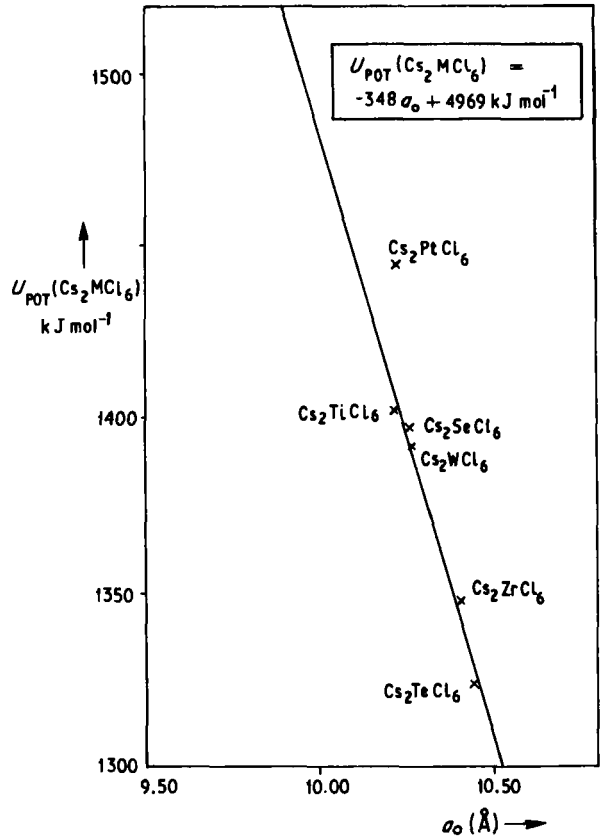


FIG. 8. Calculated lattice energy for cesium salts, Cs_2MCl_6, as a function of the cubic cell parameter, a_0. The relationship $U_{POT}(Cs_2MCl_6) = -348a_0 + 4969$ kJ mol^{-1} is found.

Equations (53)–(56) are used in cases where no u parameter is available for the antifluorite structure. (This is the case where only powder diffraction work has been carried out.)

IV. Thermochemical Data

The following standard thermodynamic data are used consistently throughout this study.

$$\Delta H_f^{\theta}(K^+)(g) = 514.2 \text{ kJ mol}^{-1} \textit{ (34)}^* \tag{57}$$

$$\Delta H_f^{\theta}(Rb^+)(g) = 494.9 \text{ kJ mol}^{-1} \textit{ (61)} \tag{58}$$

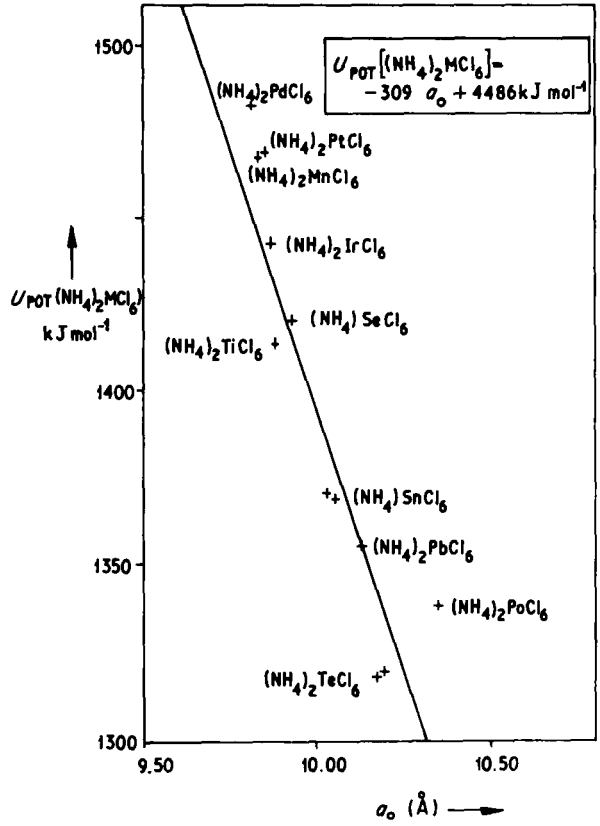


FIG. 9. Calculated lattice energy for ammonium salts, $(NH_4)_2MCl_6$, as a function of the cubic cell parameter, a_0. The relationship $U_{POT}[(NH_4)_2MCl_6] = -309a_0 + 4486$ kJ mol^{-1} is found.

$$\Delta H_f^{\theta}(Cs^+)(g) = 452.3 \text{ kJ mol}^{-1} \textit{ (34)} \tag{59}$$

$$\Delta H_f^{\theta}(Tl^+)(g) = 777.7 \text{ kJ mol}^{-1} \textit{ (56)} \tag{60}$$

$$\Delta H_f^{\theta}(NH_4^+)(g) = 630.2 \text{ kJ mol}^{-1} \textit{ (37)} \tag{61}$$

$$\Delta H_f^{\theta}(F^-)(g) = -270.7 \text{ kJ mol}^{-1} \textit{ (11)} \tag{62}$$

$$\Delta H_f^{\theta}(Cl^-)(g) = -246.0 \text{ kJ mol}^{-1} \textit{ (11)} \tag{63}$$

$$\Delta H_f^{\theta}(Br^-)(g) = -233.9 \text{ kJ mol}^{-1} \textit{ (11)} \tag{64}$$

$$\Delta H_f^{\theta}(H^+)(g) = 1536.2 \text{ kJ mol}^{-1} \text{ (56)} \quad (65)$$

$$\Delta H_{hyd}^{\theta}(H^+)(g) = -1100.6 \text{ kJ mol}^{-1} \text{ (37)} \quad (66)$$

Other thermochemical data used in the course of this study are cited at the relevant point in the text; the above data are the more general and heavily used data.

V. Computations of Lattice Energies and Associated Data

A. Format

This chapter cites data extracted from the literature (structural information, standard enthalpies of formation, etc.), and from these data much new thermodynamic information is derived. To make the immediate distinction between these two sets of data, we have adopted the policy of enclosing within boxes the *derived* data included in this study.

The entry for a given ion is divided where appropriate into three subsections. The subsection "*Recent Studies*" give the results obtained by Jenkins and Pratt using their recently proposed (*39*) minimization technique (Section II,A) for lattice energies and the associated thermochemical values. The new data derived from such calculations are enclosed in boxes. Using the accurately computed lattice energies from subsections *a*, we can derive the plots given in Fig. 6–9 [and the associated least squares-fit equations, (53)–(56)] from which, in cases where only a_0 is known for an antifluorite structure, $U_{POT}(A_2MX_6)$ can be interpolated. The subsection which lists these results is headed "*Derived Estimates.*" We give in Table I the numerical values of the lattice energy, etc., as derived from other work and we list thermochemical values cited in these studies in subsections headed "*Previous Calculations.*"

The numerical results from subsections *a*, *b*, and *c* are collected in Tables III, IV, and I, respectively.

Absence of a subsection for a given ion implies that the appropriate section was not relevant to that particular ion, usually because of lack of the necessary data.

The compounds are dealt with in periodic order. A standard format for the presentation of the results is established for $TiCl_6^{2-}$, and the results for the ions subsequently dealt with are presented in an abbreviated but similar fashion.

TABLE IV

DERIVED ESTIMATES FOR LATTICE ENERGIES USING EQUATIONS (53)–(56) IN THE TEXT

MX_6^{2-}	A^+	a_0 (Å)	$U_{POT}(A_2MX_6)$ (kJ mol^{-1})
$ZrCl_6^{2-}$	K^+	10.08	1339
$HfCl_6^{2-}$	K^+	10.06	1345
$NbCl_6^{2-}$	K^+	9.97	1375
	Rb^+	10.10	1371
	Cs^+	10.31	1381
$TaCl_6^{2-}$	K^+	9.96	1378
	Rb^+	10.11	1368
	Cs^+	10.32	1378
$MoCl_6^{2-}$	Rb^+	9.99	1408
	Cs^+	10.27	1395
$MnCl_6^{2-}$	Cs^+	10.17	1430
$TcCl_6^{2-}$	Rb^+	9.965	1417
$ReCl_6^{2-}$	Rb^+	9.974	1414
	Cs^+	10.26	1398
	NH_4^+	9.98	1402
	NH_4^+	10.07	1374
$RuCl_6^{2-}$	K^+	9.738	1451
$OsCl_6^{2-}$	Cs^+	10.230	1409
	NH_4^+	9.881	1433
$PdCl_6^{2-}$	K^+	9.74	1450
	Rb^+	9.87	1449
	Cs^+	10.18	1426
$SbCl_6^{2-}$	Rb^+	10.14	1357
$TeCl_6^{2-}$	K^+	10.143	1318

B. TITANIUM(IV), ZIRCONIUM(IV), AND HAFNIUM(IV) SALTS

1. $TiCl_6^{2-}$: *Hexachlorotitinate Ion*

a. Recent Studies

i. *Structures.* The hexachlorotitinates that possess the antifluorite structure and for which complete structural information is available are

K_2TiCl_6 (a_0 = 9.792 Å, u = 0.24) (*74*)

Rb_2TiCl_6 (a_0 = 9.922 Å, u = 0.235) (*74*)

Cs_2TiCl_6 (a_0 = 10.219 Å, u = 0.23) (*74*)

$(NH_4)_2TiCl_6$ (a_0 = 9.89 Å, u = 0.24) (*74*)

ii. *Charge distribution in ion.* We use, in the absence of experimental data, the method of Jørgensen (*42–45*) to establish

$$\boxed{q_{Cl} = -0.61}$$

iii. *Lattice energies.* Based on a charge distribution above, we calculate the total lattice potential energies of the salts concerned to be

$$\boxed{\begin{aligned} U_{POT}(K_2TiCl_6) &= 1412 \text{ kJ mol}^{-1} \\ U_{POT}(Rb_2TiCl_6) &= 1415 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2TiCl_6) &= 1402 \text{ kJ mol}^{-1} \\ U_{POT}[(NH_4)_2TiCl_6] &= 1413 \text{ kJ mol}^{-1} \end{aligned}}$$

iv. *"Basic" radius.* The values of $\bar{r}_{TiCl_6^{2-}}$ given in Fig. 10 and corresponding to $q_{Cl} = -0.61$ are 2.48 Å (K_2TiCl_6); 2.47 Å (Rb_2TiCl_6); 2.50 Å (Cs_2TiCl_6), and 2.50 Å [$(NH_4)_2TiCl_6$]. They average to:

$$\boxed{\bar{r}_{TiCl_6^{2-}} = 2.48 \text{ Å}}$$

v. *Enthalpy of formation of gaseous* $TiCl_6^{2-}$ *ion.* Korol'kov and Efimov (*48*) have reported the enthalpies of formation of A_2MX_6 salts (A = K, Rb, Cs; M = Ti; X = Cl) from their *gaseous atoms*, ΔH_1:

$$2A(g) + Ti(g) + 6Cl(g) \xrightarrow{\Delta H_1} A_2TiCl_6(c)$$

This enthalpy is related to $\Delta H_f^\theta(A_2TiCl_6)(c)$ by the equation:

$$\Delta H_f^\theta(A_2TiCl_6)(c) = \Delta H_1 + 2\Delta H_f^\theta(A)(g) + \Delta H_f^\theta(Ti)(g) + 6\Delta H_f^\theta(Cl)(g) \tag{67}$$

where: $\Delta H_f^\theta(K)(g) = 89.16$ kJ mol^{-1} (*34*), $\Delta H_f^\theta(Rb)(g) = 85.8$ kJ mol^{-1} (*61*), $\Delta H_f^\theta(Cs)(g) = 76.65$ kJ mol^{-1} (*34*), $\Delta H_f^\theta(Ti)(g) = 473$ kJ mol^{-1} (*34*), and $\Delta H_f^\theta(Cl)(g) = 121.01$ kJ mol^{-1} (*34*); and we find that

$$\begin{aligned} \Delta H_f^\theta(K_2TiCl_6)(c) &= -1747 \text{ kJ mol}^{-1} \\ \Delta H_f^\theta(Rb_2TiCl_6)(c) &= -1767 \text{ kJ mol}^{-1} \\ \Delta H_f^\theta(Cs_2TiCl_6)(c) &= -1797 \text{ kJ mol}^{-1} \end{aligned}$$

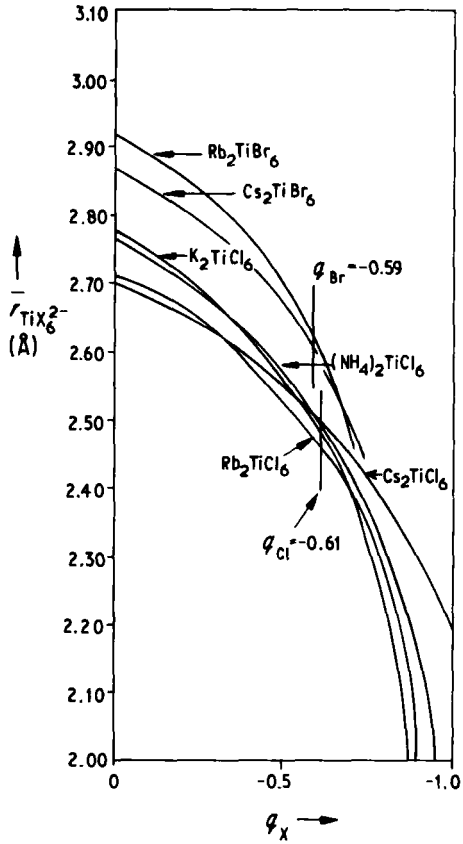


FIG. 10. Basic radius of $TiCl_6^{2-}$ and $TiBr_6^{2-}$ ions, corresponding to lattice potential energy minima, as a function of the charge, q_X, on the halogen atom.

Using the standard data at the end of the last section in Eq. (1) with the computed values of $U_{POT}(A_2TiCl_6)$, we can plot $\Delta H_f^\theta(TiCl_6^{2-})(g)$ as a function of q_{Cl} (Fig. 11). We find that $\Delta H_f^\theta(TiCl_6^{2-})(g) = -1361$ kJ mol^{-1} (K_2TiCl_6), $= -1342$ kJ mol^{-1} (Rb_2TiCl_6) and -1300 kJ mol^{-1} (Cs_2TiCl_6), giving an estimated average value:

$$\Delta H_f^\theta(TiCl_6^{2-})(g) = -1330 \pm 30 \text{ kJ mol}^{-1}$$

vi. *Enthalpy of hydration of the gaseous* $TiCl_6^{2-}$ *ion.* No aqueous data exist for these salts.

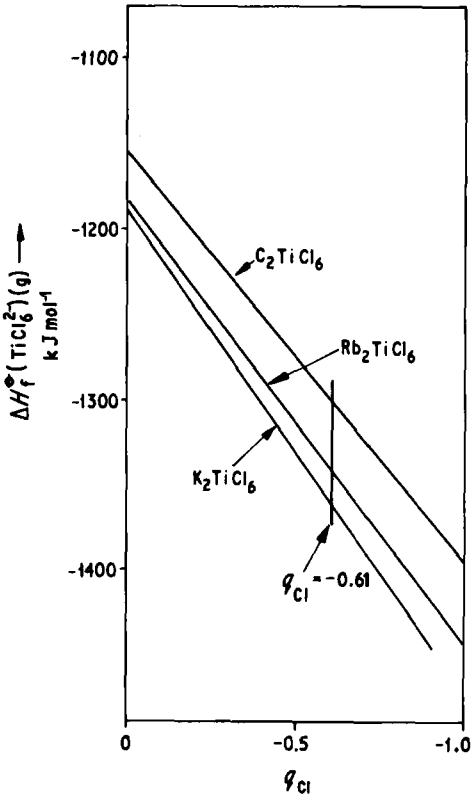


FIG. 11. Enthalpy of formation, $\Delta H_f^\theta(TiCl_6^{2-})(g)$ corresponding to lattice potential energy minimum as a function of the charge, q_{Cl} on the chlorine atoms.

vii. *Halide ion affinities.* Taking $\Delta H_f^\theta(TiCl_4)(g) = -763.2$ kJ mol^{-1} (*56*); $\Delta H_f^\theta(TiCl_4)(l) = -804.2$ kJ mol^{-1} (*56*), we find:

$$\Delta H_{Cl(g)} = -76 \pm 30 \text{ kJ mol}^{-1}$$
$$\Delta H_{Cl(l)} = -36 \pm 30 \text{ kJ mol}^{-1}$$

for the chloride ion affinities of $TiCl_4(g)$ and $TiCl_4(1)$, respectively.

viii. *Prediction of lattice energies.* Taking

$$\Delta H_f^\theta(Tl_2TiCl_6)(c) = -1330 \text{ kJ mol}^{-1} \text{ (56)},$$

we calculate:

$$\boxed{U_{POT}(Tl_2TiCl_6) = 1560 \pm 30 \text{ kJ mol}^{-1}}$$

2. $TiBr_6^{2-}$: *Hexabromotitinate Ion*

a. Recent Studies

i. *Structure*

Rb_2TiBr_6 ($a_0 = 10.39$ Å, $u = 0.25$) (*48*)

Cs_2TiBr_6 ($a_0 = 10.57$ Å, $u = 0.25$) (*48*)

ii. *Charge distribution*

$$q_{Br} = -0.59$$

iii. *Lattice energies*

$$\boxed{\begin{aligned} U_{POT}(Rb_2TiBr_6) &= 1341 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2TiBr_6) &= 1339 \text{ kJ mol}^{-1} \end{aligned}}$$

iv. "*Basic*" *radius of ion* (Fig. 10)

$$\boxed{\bar{r}_{TiBr_6^{2-}} = 2.61 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion* (Fig. 12)
Ancillary data:

$$\Delta H_f^{\theta}(K_2TiBr_6)(c) = -1493 \text{ kJ mol}^{-1} \text{ (48)};$$

$\Delta H_f^{\theta}(Rb_2TiBr_6)(c) = -1517$ kJ mo $^{-1}$ (*48*), -1505 kJ mol^{-1} (*68a*) or -1612 kJ mol^{-1} (*64*), (*62a*) and $\Delta H_f^{\theta}(Cs_2TiBr_6)(c) = -1553$ kJ mol^{-1} (*48*), -1644 kJ mol^{-1} (*62a*) or -1641 kJ mol^{-1} (*64*). Where two values are given, the former has been calculated by us from the $\Delta H_f^{a}(A_2MBr_6)(c)$ data of Korol'kov and Efimov using $\Delta H_f^{0}(Br)(g) = 111.9$ kJ mol^{-1} (*34*), similar to the case of the corresponding chlorides, A_2MCl_6. We have chosen to use these formation data because they were recorded two years later than the alternative data available.

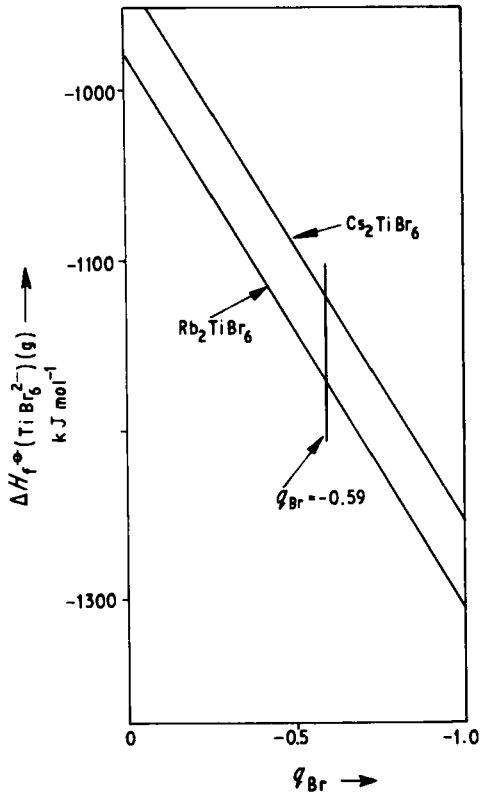


FIG. 12. Enthalpy of formation, $\Delta H_f^{\theta}(TiBr_6^{2-})(g)$, corresponding to lattice potential energy minimum, as a function of the charge, q_{Br}, on the bromine atom.

Assigned value:

$$\boxed{\Delta H_f^{\theta}(TiBr_6^{2-})(g) = -1142 \pm 32 \text{ kJ mol}^{-1}}$$

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(TiBr_4)(c) = -616.7 \text{ kJ mol}^{-1} \ (56)$$

and

$$\Delta H_f^{\theta}(TiBr_4)(g) = -549.3 \text{ kJ mol}^{-1} \ (56).$$

Assigned value:

$$\boxed{\begin{aligned}\Delta H_{Br(c)} &= -58 \pm 32 \text{ kJ mol}^{-1}\\ \Delta H_{Br(g)} &= -125 \pm 32 \text{ kJ mol}^{-1}\end{aligned}}$$

vii. *Prediction of lattice energies*
Ancillary data:

$$\Delta H_f^{\theta}(K_2TiBr_6)(c) = -1493 \text{ kJ mol}^{-1} \text{ (48)}$$

and

$$\Delta H_f^{\theta}(TiBr_6^{2-})(g) = -1142 \pm 32 \text{ kJ mol}^{-1}.$$

Assigned value:

$$\boxed{U_{POT}(K_2TiBr_6) = 1379 \pm 32 \text{ kJ mol}^{-1}}$$

3. $ZrCl_6^{2-}$: *Hexachlorozirconate Ion*

a. Recent Studies

i. *Structures*

Rb_2ZrCl_6 ($a_0 = 10.178$ Å, $u = 0.24$) (*74*)
Cs_2ZrCl_6 ($a_0 = 10.407$ Å, $u = 0.235$) (*74*)

ii. *Charge distribution*

$$q_{Cl} = -0.66$$

iii. *Lattice energy*

$$\boxed{\begin{aligned}U_{POT}(Rb_2ZrCl_6) &= 1348 \text{ kJ mol}^{-1}\\ U_{POT}(Cs_2ZrCl_6) &= 1348 \text{ kJ mol}^{-1}\end{aligned}}$$

iv. "*Basic*" *radius of ion* (Fig. 13)

$$\boxed{\bar{r}_{ZrCl_6^{2-}} = 2.47 \text{ Å}}$$

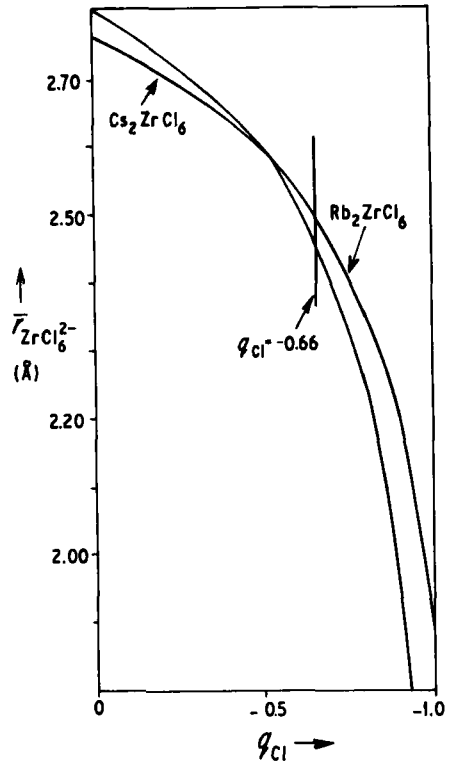


FIG. 13. Basic radius of $ZrCl_6^{2-}$ ion, corresponding to lattice potential energy minimum, as a function of the charge, q_{Cl}, on the chlorine atoms.

v. *Enthalpy of formation of gaseous ion*

Ancillary data: $\Delta H_f^\theta(Zr)(g) = 620$ kJ mol^{-1} (*34*), together with Korol'kov and Efimov's (*48*) estimate of the enthalpy of formation of Cs_2ZrCl_6 to be -3445 kJ mol^{-1} (from gaseous atoms)

Assigned value:

$$\boxed{\Delta H_f^\theta(ZrCl_6^{2-})(g) = -1503 \text{ kJ mol}^{-1}}$$

Gelbman and Westland (*22*) have reported $\Delta H_f^\theta(Cs_2ZrCl_6)(c) = -1992 \pm 4$ kJ mol^{-1} and combining this with the calculated lattice energy above we obtain a value: $\Delta H_f^\theta(ZrCl_6^{2-})(g) = -1549$ kJ mol^{-1}.

Further using Gelbman and Westland's (*22*) value for

$$\Delta H_f^\theta(K_2ZrCl_6)(c) = -1932 \pm 4 \text{ kJ mol}^{-1}$$

in conjunction with the lattice energy $U_{POT}(K_2ZrCl_6)$ estimated below, we find:

$$\Delta H_f^{\theta}(ZrCl_6^{2-})(g) \simeq -1621 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta H_f^{\theta}(ZrCl_6^{2-})(g) = -1526 + 32 \text{ kJ mol}^{-1}}$$

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(ZrCl_4)(c) = -980.5 \text{ kJ mol}^{-1} \text{ (22, 56)}$$

and

$$\Delta H_f^{\theta}(ZrCl_4)(g) = -870.3 \text{ kJ mol}^{-1} \text{ (56)}.$$

Assigned values:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -54 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -164 \text{ kJ mol}^{-1} \end{aligned}}$$

b. Derived Estimates. The above calculations are derived from our accurate approach to the treatment of lattice energies. In addition, on the basis of partial structural details:

$$K_2ZrCl_6 \ (a_0 = 10.08 \text{ Å}) \text{ (54)}$$

we can use Eq. (53) to estimate

$$\boxed{U_{POT}(K_2ZrCl_6) \simeq 1339 \text{ kJ mol}^{-1}}$$

c. Previous Calculations. Gelbman and Westland (*22*) have cited the relationship:

$$\overline{\Delta H}_{Cl(g)} = -1597 \pm 5 + U_{POT}(K_2ZrCl_6) \text{ kJ mol}^{-1} \qquad (68)$$

In his previous work (*51*) with Lal, Westland quoted:

$$U_{POT}(K_2NbCl_6) = 1586 \text{ kJ mol}^{-1}$$

and in the present work (*22*) he quotes:

$$U_{POT}(K_2NbCl_6) - U_{POT}(K_2ZrCl_6) \simeq 15 \text{ kJ mol}^{-1} \quad (69)$$

on the basis of Kapustinskii's equation (*46*) whereupon:

$$U_{POT}(K_2ZrCl_6) \simeq 1571 \text{ kJ mol}^{-1}$$

and hence a chloride ion affinity for $ZrCl_4$(g) of

$$\overline{\Delta H}_{Cl(g)} = -26 \pm 5 \text{ kJ mol}^{-1}$$

is predicted.

4. $ZrBr_6^{2-}$: *Hexabromozirconate Ion*

c. Previous Calculations. Makhija and Westland (*54a*) have cited the relationships:

$$\overline{\Delta H}_{Br(g)} = -1510 + U_{POT}(K_2ZrBr_6) \text{ kJ mol}^{-1} \quad (70)$$

$$\overline{\Delta H}_{Br(g)} = -1465 + U_{POT}(Cs_2ZrBr_6) \text{ kJ mol}^{-1} \quad (71)$$

Using their lattice energies cited in Table I they obtain:

$$\overline{\Delta H}_{Br(g)} = -9 \text{ or } -1 \text{ kJ mol}^{-1}$$

5. $HfCl_6^{2-}$: *Hexachlorohafnate Ion*

a. Recent Studies.

i. *Structures*

$$Cs_2HfCl_6 \ (a_0 = 10.42 \text{ Å}, u = 0.25) \ (54c)$$

ii. *Charge distribution*

$$q_{Cl} = -0.66$$

iii. *Lattice energies*

$$\boxed{U_{POT}(Cs_2HfCl_6) = 1315 \text{ kJ mol}^{-1}}$$

iv. *"Basic" radius of ion*

$$\boxed{\bar{r}_{HfCl_6^{2-}} = 2.37 \text{ Å}}$$

No thermochemical data exists for this salt.

b. Derived Estimates

i. *Structures*

K_2HfCl_6 ($a_0 = 10.06$ Å) (*22*, *71*)

ii. *Prediction of lattice energies*
Assigned value:

$$\boxed{U_{POT}(K_2HfCl_6) \simeq 1345 \text{ kJ mol}^{-1}}$$

iii. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2HfCl_6)(c) = -1957 \pm 12 \text{ kJ mol}^{-1} \text{ (22)}$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(HfCl_6^{2-})(g) = -1640 \pm 12 \text{ kJ mol}^{-1}}$$

iv. *Halide ion affinites*
Ancillary data:

$$\Delta H_f^{\theta}(HfCl_4)(c) = -990 \pm 10 \text{ kJ mol}^{-1} \text{ (56)}, -992 \text{ kJ mol}^{-1} \text{ (20b)}$$

and

$$\Delta H_f^{\theta}(HfCl_4)(g) = -889 \pm 12 \text{ kJ mol}^{-1} \text{ (56)}.$$

Assigned value:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -158 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -259 \text{ kJ mol}^{-1} \end{aligned}}$$

c. Previous Calculations. Gelbman and Westland (*22*) have cited the relationship

$$\overline{\Delta H}_{Cl(g)} = -1611 \pm 14 + U_{POT}(K_2HfCl_6)\ \text{kJ mol}^{-1} \tag{72}$$

and the lattice energy relationship

$$U_{POT}(K_2HfCl_6) - U_{POT}(K_2ZrCl_6) \simeq 3\ \text{kJ mol}^{-1} \tag{73}$$

Using the lattice energy of K_2ZrCl_6, which they obtained ($\simeq 1571$ kJ mol^{-1}) (*22*), they would assign

$$U_{POT}(K_2HfCl_6) \simeq 1574\ \text{kJ mol}^{-1}$$

and

$$\overline{\Delta H}_{Cl(g)} \simeq -37 \pm 14\ \text{kJ mol}^{-1}$$

6. $HfBr_6^{2-}$: *Hexabromohafnate Ion*

c. Previous Calculations: Makhija and Westland (*54a*) have given the relationship:

$$\overline{\Delta H}_{Br(g)} = -1510 = U_{POT}(Cs_2HfBr_6)\ \text{kJ mol}^{-1} \tag{74}$$

Using their lattice energy given in Table I:

$$\overline{\Delta H}_{Br(g)} = -46\ \text{kJ mol}^{-1}$$

C. Niobium(IV) and Tantalum(IV) Salts

1. $NbCl_6^{2-}$ *Hexachloroniobate Ion*

a. Recent Studies. No crystal structure data are available.

b. Derived Estimates

i. *Structures*

K_2NbCl_6 ($a_0 = 9.97$ Å) (*51*)

Rb_2NbCl_6 ($a_0 = 10.10$ Å) (*51*)

Cs_2NbCl_6 ($a_0 = 10.31$ Å) (*51*)

ii. *Prediction of lattice energies*
Assigned values:

$$\boxed{\begin{aligned} U_{POT}(K_2NbCl_6) &= 1375 \text{ kJ mol}^{-1} \\ U_{POT}(Rb_2NbCl_6) &= 1371 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2NbCl_6) &= 1381 \text{ kJ mol}^{-1} \end{aligned}}$$

iii. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2NbCl_6)(c) = -1594 \text{ kJ mol}^{-1} \text{ (51)},$$
$$\Delta H_f^{\theta}(Rb_2NbCl_6)(c) = -1619 \text{ kJ mol}^{-1} \text{ (51)},$$

and

$$\Delta H_f^{\theta}(Cs_2NbCl_6)(c) = -1663 \text{ kJ mol}^{-1} \text{ (51)}.$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(NbCl_6^{2-})(g) = -1224 \pm 32 \text{ kJ mol}^{-1}}$$

iv. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(NbCl_4)(c) = -694 \text{ kJ mol}^{-1} \text{ (34)}$$

and

$$\Delta H_f^{\theta}(NbCl_4)(g) = -561 \text{ kJ mol}^{-1} \text{ (34)}.$$

Assigned value:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -38 \quad 32 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -171 \pm 32 \text{ kJ mol}^{-1} \end{aligned}}$$

c. Previous Calculations. Lal and Westland (*51*) have cited the relationship.

$$\overline{\Delta H}_{Cl(g)} = -1571 + U_{POT}(K_2NbCl_6) \qquad (75)$$

together with the following lattice energies obtained from the Kapustinskii (*46*) equation:

$$U_{POT}(K_2NbCl_6) = 1586 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2NbCl_6) = 1569 \text{ kJ mol}^{-1}$$
$$U_{POT}(CsNbCl_6) = 1540 \text{ kJ mol}^{-1}$$

Using the first of these values in Eq. (76), the predicted chloride ion affinity of niobium(IV) chloride is therefore:

$$\overline{\Delta H}_{Cl(g)} = +15 \text{ kJ mol}^{-1}$$

2. $TaCl_6^{2-}$: *Hexachlorotantalate Ion*

a. Recent Studies. No crystal structure data are available.

b. Derived Estimates

i. *Structures*

K_2TaCl_6 ($a_0 = 9.96$ Å) (*51*)
Rb_2TaCl_6 ($a_0 = 10.11$ Å) (*51*)
Cs_2TaCl_6 ($a_0 = 10.32$ Å) (*51*)

ii. *Prediction of lattice energies*
Assigned value:

$$U_{POT}(K_2TaCl_6) = 1378 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2TaCl_6) = 1368 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2TaCl_6) = 1378 \text{ kJ mol}^{-1}$$

iii. *Enthalpy of formation of gaseous ion*
Ancillary data:

$\Delta H_f^{\theta}(K_2TaCl_6)(c) = -1648 \text{ kJ mol}^{-1}$ (*51*) or $-1707 \text{ kJ mol}^{-1}$ (*68*),
$\Delta H_f^{\theta}(Rb_2TaCl_6)(c) = -1669 \text{ kJ mol}^{-1}$ (*51*),

and

$$\Delta H_f^{\theta}(Cs_2TaCl_6)(c) = -1711 \text{ kJ mol}^{-1} \text{ (51)}.$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(TaCl_6^{2-})(g) = -1296 \pm 49 \text{ kJ mol}^{-1}}$$

iv. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(TaCl_4)(c) = -702 \text{ kJ mol}^{-1} \text{ (34)*}, -860 \text{ kJ mol}^{-} \text{ (20a)}$$

and

$$\Delta H_f^{\theta}(TaCl_4)(g) = -561 \text{ kJ mol}^{-1} \text{ (34)}.$$

Assigned value:

$$\boxed{\begin{aligned}\overline{\Delta H}_{Cl(c)} &= -102 \pm 49 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -243 \pm 49 \text{ kJ mol}^{-1}\end{aligned}}$$

c. Previous Calculations. Tsintsius and Smirnova (*68*) have calculated that:

$$\Delta H_f^{\theta}(TaCl_6^{2-})(g) = -1268 \text{ kJ mol}^{-1}$$

from lattice energies obtained from the extended Kapustinskii (*46*) equation:

$$U_{POT}(K_2TaCl_6) = 1582 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2TaCl_6) = 1565 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2TaCl_6) = 1540 \text{ kJ mol}^{-1}$$

Lal and Westland (*51*) have cited the relationship

$$\overline{\Delta H}_{Cl(g)} = -1609 + U_{POT}(K_2TaCl_6) \qquad (76)$$

together with the following lattice energies obtained from the Kapustinskii (*46*) relationship:

$$U_{POT}(K_2TaCl_6) = 1586 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2TaCl_6) = 1569 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2TaCl_6) = 1540 \text{ kJ mol}^{-1}$$

* Preferred value.

Using the first of these values in Eq. (77), the predicted chloride ion affinity of tantalum(IV) chloride is therefore:

$$\overline{\Delta H}_{Cl(g)} = -23 \text{ kJ mol}^{-1}$$

D. Chromium(IV), Molybdenum(IV) and Tungsten(IV) Salts

1. CrF_6^{2-}: *Hexafluorochromate Ion*

a. Recent Studies

i. *Structure*

$$Cs_2CrF_6 \ (a_0 = 9.02 \text{ Å}, u = 0.192) \ (74)$$

ii. *Charge distribution*

$$q_F = -0.65$$

iii. *Lattice energies.* The equation for the lattice potential energy of Cs_2CrF_6 as a function of the charge q_F takes the rectilinear form:

$$U_{POT}(Cs_2CrF_6) \simeq 120 \ q_F + 1681 \text{ kJ mol}^{-1}$$

and corresponding to $q_F = -0.65$,

$$\boxed{U_{POT}(Cs_2CrF_6) = 1603 \text{ kJ mol}^{-1}}$$

iv. *"Basic" radius of ion*

$$\boxed{\bar{r}_{CrF_6^{2-}} = 2.08 \text{ Å}}$$

No thermochemical data exist for A_2CrF_6 salts.

2. $MoCl_6^{2-}$: *Hexachloromolybdate Ion*

a. Recent Studies

i. *Structure*

$$K_2MoCl_6 \ (a_0 = 9.85 \text{ Å}, u = 0.234) \ (74)$$

ii. *Charge distribution*

$$q_{Cl} = -0.60$$

iii. *Lattice energies*

$$\boxed{U_{POT}(K_2MoCl_6) = 1418 \text{ kJ mol}^{-1}}$$

iv. *"Basic" radius of ion*

$$\boxed{\bar{r}_{MoCl_6^{2-}} = 2.54 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2MoCl_6)(c) = -1475 \text{ kJ mol}^{-1} (11), -1465 \text{ kJ mol}^{-1} \quad (48)$$

or

$$-1469 \text{ kJ mol}^{-1} (19).$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(MoCl_6^{2-})(g) = -1070 \pm 5 \text{ kJ mol}^{-1}}$$

iv. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(MoCl_4)(c) = -475.8 \text{ kJ mol}^{-1} (11)$$

and

$$\Delta H_f^{\theta}(MoCl_4)(g) = -386.3 \text{ kJ mol}^{-1} (11)$$

Assigned value:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -102 \pm 5 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -192 \pm 5 \text{ kJ mol}^{-1} \end{aligned}}$$

vii. *Prediction of lattice energies*
Ancillary data:

$$\Delta H_f^{\theta}(Rb_2MoCl_6)(c) = -1479 \text{ kJ mol}^{-1} \text{ (48)}$$

or -1495 kJ mol^{-1} (*19*);

$$\Delta H_f^{\theta}(Cs_2MoCl_6)(c) = -1512 \text{ kJ mol}^{-1} \text{ (48)}$$

or -1527 kJ mol^{-1} (*19*); and

$$\Delta H_f^{\theta}(Na_2MoCl_6)(c) = -1376 \text{ kJ mol}^{-1} \text{ (11)}$$

or -1372 kJ mol^{-1} (*19*).
Assigned values:

$$U_{POT}(Rb_2MoCl_6) = 1399 \text{ kJ mol}^{-1} \text{ or } 1383 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2MoCl_6) = 1347 \text{ kJ mol}^{-1} \text{ or } 1332 \text{ kJ mol}^{-1}$$
$$U_{POT}(Na_2MoCl_6) = 1526 \text{ kJ mol}^{-1} \text{ or } 1530 \text{ kJ mol}^{-1}$$

depending on the source used for $\Delta H_f^{\theta}(A_2MoCl_6)(c)$.

b. Derived Values

i. *Structures*

Rb_2MoCl_6 ($a_0 = 9.99$ Å) (*74*)
Cs_2MoCl_6 ($a_0 = 10.27$ Å) (*74*)

ii. *Prediction of lattice energies*
Assigned value:

$$U_{POT}(Rb_2MoCl_6) = 1408 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2MoCl_6) = 1395 \text{ kJ mol}^{-1}$$

iii. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(Rb_2MoCl_6)(c) = -1479 \text{ kJ mol}^{-1} \text{ (48)}$$

or -1495 kJ mol^{-1} (*19*); and

$$\Delta H_f^{\theta}(Cs_2MoCl_6)(c) = -1512 \text{ kJ mol}^{-1} \text{ (48)}$$

or -1527 kJ mol^{-1} (*19*).

Assigned value:

$$\boxed{\Delta H_f^{\theta}(MoCl_6^{2-})(g) = -1041 \pm 28 \text{ kJ mol}^{-1}}$$

iv. *Halide ion affinities*

Ancillary data:

$$\Delta H_f^{\theta}(MoCl_4)(c) = -475.8 \text{ kJ mol}^{-1} \text{ (11)}$$

and

$$\Delta H_f^{\theta}(MoCl_4)(g) = -386.3 \text{ kJ mol}^{-1} \text{ (11)}.$$

Assigned value:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -73 \pm 28 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -163 \pm 28 \text{ kJ mol}^{-1} \end{aligned}}$$

c. Previous Calculations. Efimov and Belorukova (*19*), using the extended Kapustinskii equation, have obtained:

$$U_{POT}(Na_2MoCl_6) = 1638 \text{ kJ mol}^{-1}$$

$$U_{POT}(K_2MoCl_6) = 1602 \text{ kJ mol}^{-1}$$

$$U_{POT}(Rb_2MoCl_6) = 1567 \text{ kJ mol}^{-1}$$

$$U_{POT}(Cs_2MoCl_6) = 1537 \text{ kJ mol}^{-1}$$

from which they obtained:

$$\Delta H_f^{\theta}(MoCl_6^{2-})(g) = -1023 \text{ kJ mol}^{-1}$$

3. WCl_6^{2-}: *Hexachlorotungstate Ion*

a. Recent Studies

i. *Structures*

K_2WCl_6 ($a_0 = 9.875$ Å, $u = 0.239$) (*47,57*)

Rb_2WCl_6 ($a_0 = 10.0$ Å, $u = 0.236$) (*47,57*)

Cs_2WCl_6 ($a_0 = 10.27$ Å, $u = 0.230$) (*47,57*)

ii. *Charge distribution*

$$q_{Cl} = -0.62$$

iii. *Lattice energies*

$$U_{POT}(K_2WCl_6) = 1398 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2WCl_6) = 1397 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2WCl_6) = 1392 \text{ kJ mol}^{-1}$$

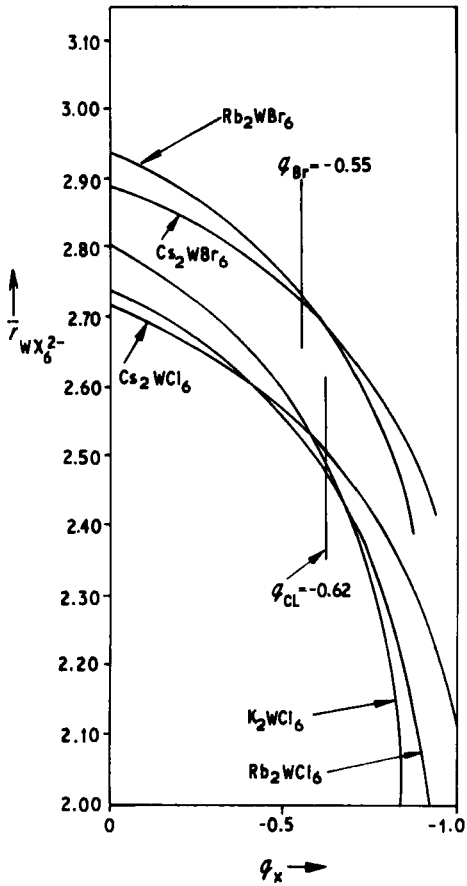


FIG. 14. Basic radii for ions WCl_6^{2-} and WBr_6^{2-}, corresponding to lattice potential energy minima, as a function of the charge, q_X, on the halogen atoms.

iv. *"Basic" radius of ion* (Fig. 14)

$$\bar{r}_{WCl_6^{2-}} = 2.49 \text{ Å}$$

v. *Enthalpy of formation of gaseous ion* (Fig. 15)
Ancillary data:

$$\Delta H_f^\theta(K_2WCl_6)(c) = -1380 \text{ kJ mol}^{-1} (57),$$

and

$$-1359 \text{ kJ mol}^{-1} (11, 49), \Delta H_f^\theta(Rb_2WCl_6)(c) = -1429 \text{ kJ mol}^{-1} (11, 49),$$
$$\Delta H_f^\theta(Cs_2WCl_6)(c) = -1446 \text{ kJ mol}^{-1} (11, 49).$$

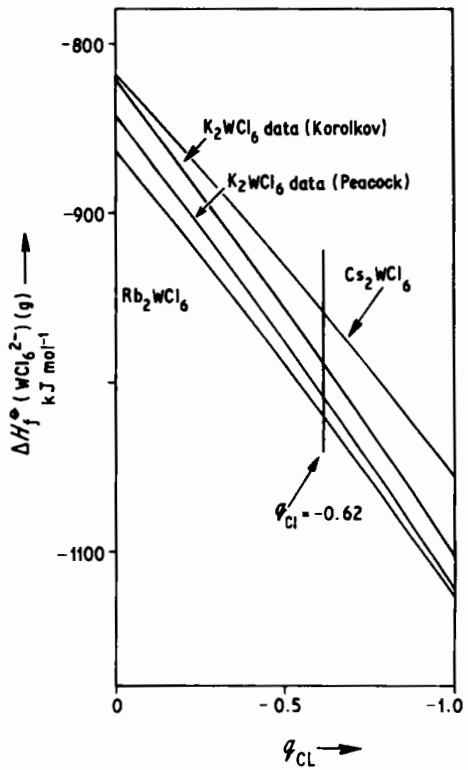


FIG. 15. Enthalpy of formation, $\Delta H_f^\theta(WCl_6^{2-})(g)$, corresponding to the lattice potential energy minima, as a function of the charge q_{Cl} on the chlorine atom.

Assigned value:

$$\boxed{\Delta H_f^{\theta}(WCl_6^{2-})(g) = -985 \pm 35 \text{ kJ mol}^{-1}}$$

vi. *Halide ion affinities*

Ancilliary data:

$$\Delta H_f^{\theta}(WCl_4)(c) = -447 \text{ kJ mol}^{-1} \ (11)$$

or -469 kJ mol^{-1} (*56*) and

$$\Delta H_f^{\theta}(WCl_4)(g) = -341 \text{ kJ mol}^{-1} \ (11)$$

or -305 kJ mol^{-1} (*56*).

Assigned values:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -46 \pm 35 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -152 \pm 35 \text{ kJ mol}^{-1} \end{aligned}}$$

The values above correspond to the CATCH (*11*) data, taken since it emerges from a later tabulation.

vii. *Prediction of electron affinity of* $WCl_6(g)$: Taking

$$\Delta H_f^{\theta}(WCl_6)(g) = -499 \text{ kJ mol}^{-1} \ (11),$$

we can calculate the electron affinity of $WCl_6(g)$ for two electrons and find it to be:

$$A_{WCl_6} = -486 \pm 35 \text{ kJ mol}^{-1}$$

4. WBr_6^{2-}: *Hexabromotungstate ion*

a. Recent Studies

i. *Structures*

Rb_2WBr_6 ($a_0 = 10.50$ Å, $u = 0.236$) (*47, 57*)

Cs_2WBr_6 ($a_0 = 10.70$ Å, $u = 0.232$) (*47, 57*)

ii. *Charge distribution*

$$q_{Br} = -0.55$$

iii. *Lattice energies*

$$U_{POT}(Rb_2WBr_6) = 1361 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2WBr_6) = 1362 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 14)

$$\bar{r}_{WBr_6^{2-}} = 2.72 \text{ Å}$$

v. *Enthalpy of formation of gaseous ion* (Fig. 16)
Ancillary data:

$$\Delta H_f^{\theta}(Rb_2WBr_6)(c) = -1106 \text{ kJ mol}^{-1} (57)$$

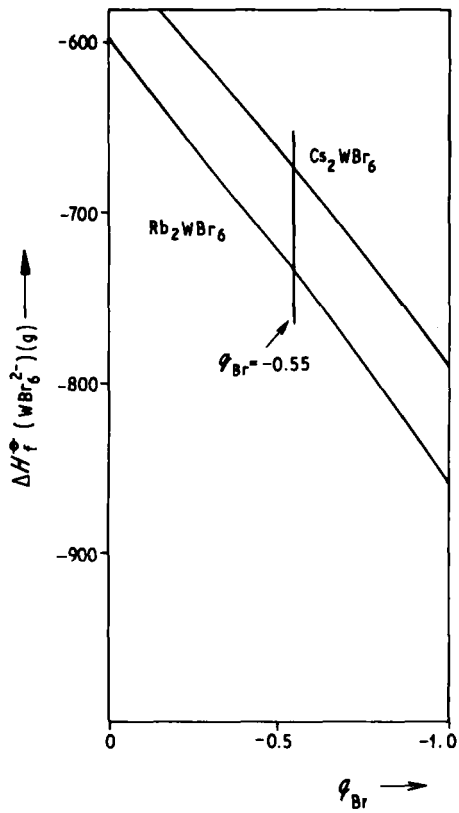


FIG. 16. Enthalpy of formation, $\Delta H_f^{\theta}(WBr_6^{2-})(g)$, corresponding to the lattice potential energy minima, as a function of the charge, q_{Br} on the bromine atom.

and

$$\Delta H_f^{\theta}(Cs_2WBr_6)(c) = -1132 \text{ kJ mol}^{-1} (57)$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(WBr_6^{2-})(g) = -705 + 30 \text{ kJ mol}^{-1}}$$

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(WBr_4)(c) = -146 \text{ kJ mol}^{-1} (61)$$

Assigned value:

$$\boxed{\overline{\Delta H}_{Br(c)} = -91 \pm 30 \text{ kJ mol}^{-1}}$$

vii. *Prediction of lattice energies*
Ancillary data:

$$\Delta H_f^{\theta}(K_2WBr_6) = -1085 \text{ kJ mol}^{-1} (57)$$

Assigned value:

$$\boxed{U_{POT}(K_2WBr_6) = 1408 \pm 30 \text{ kJ mol}^{-1}}$$

viii. *Prediction of electron affinity of* $WBr_6(c)$. In the absence of $\Delta H_f^{\theta}(WBr_6)(g)$ data we have a value for $\Delta H_f^{\theta}(WBr_6)(c)$ (*11*) and find the enthalpy change for the conversion of $WBr_6(c)$ to $WBr_6^{2-}(g)$ to be -359 ± 30 kJ mol^{-1}.

E. Manganese(IV), Technitium(IV), and Rhenium(IV) Salts

1. MnF_6^{2-}: *Hexafluoromanganate ion*

a. Recent Studies

i. *Structures*

Rb_2MnF_6 ($a_0 = 8.43$ Å, $u = 0.20$) (*74*)

Cs_2MnF_6 ($a_0 = 8.92$ Å, $u = 0.195$) (*74*)

ii. *Charge distribution*

$$q_F = -0.63$$

iii. *Lattice energies.* The curves of $U_{POT}(A_2MnF_6)$ versus q_F show a rectilinear relationship over the range $0.0 \geqslant q_F \geqslant -1.0$ and, to within 5 kJ mol^{-1}, fit the equations

$$U_{POT}(Rb_2MnF_6) \simeq 143q_F + 1778$$

$$U_{POT}(Cs_2MnF_6) \simeq 128q_F + 1701$$

For a charge of $q_F = -0.63$, we find:

$$\boxed{\begin{aligned} U_{POT}(Rb_2MnF_6) &= 1688 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2MnF_6) &= 1620 \text{ kJ mol}^{-1} \end{aligned}}$$

iv. *"Basic" radius of ion* (Fig. 17)

$$\boxed{\bar{r}_{MnCl_6^{2-}} = 2.02 \text{ Å}}$$

No thermochemical data exist for these salts.

2. $MnCl_6^{2-}$: *Hexachloromanganate ion*

a. Recent Studies

i. *Structures*

K_2MnCl_6 ($a_0 = 9.6445$ Å, $u = 0.236$) (*55*)

Rb_2MnCl_6 ($a_0 = 9.838$ Å, $u = 0.232$) (*52*)

$(NH_4)_2MnCl_6$ ($a_0 = 9.82$ Å, $u = 0.228$) (*52*)

ii. *Charge distribution*

$$q_{Cl} = -0.55$$

iii. *Lattice energies.* The curves of $U_{POT}(A_2MnCl_6)$ versus charge are not linear and vary over the range $0.0 \geqslant q_{Cl} \geqslant -1.0$ between the limits:

$$1606 \geqslant U_{POT}(K_2MnCl_6) \geqslant 1336 \text{ kJ mol}^{-1}$$

$$1583 \geqslant U_{POT}(Rb_2MnCl_6) \geqslant 1333 \text{ kJ mol}^{-1}$$

$$1588 \geqslant U_{POT}(Cs_2MnCl_6) \geqslant 1355 \text{ kJ mol}^{-1}$$

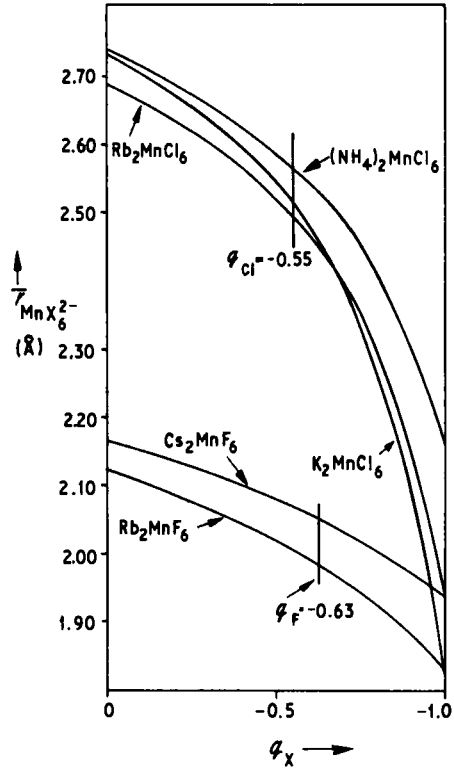


FIG. 17. Basic radii for the ions MnF_6^{2-} and $MnCl_6^{2-}$, corresponding to lattice potential energy minima, as a function of the charge, q_X, on the halogen atoms.

and assigning, on the basis that $q_{Cl} = -0.55$, we find:

$$U_{POT}(K_2MnCl_6) = 1462 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2MnCl_6) = 1451 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2MnCl_6) = 1464 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 17)

$$\bar{r}_{MnCl_6^{2-}} = 2.52 \text{ Å}$$

No thermochemical data exist for these salts.

b. Derived Estimates

i. *Structures*

$$Cs_2MnCl_6 \ (a_0 = 10.17 \text{ Å}) \ (55)$$

ii. *Prediction of lattice energies*
Assigned value:

$$\boxed{U_{POT}(Cs_2MnCl_6) = 1430 \text{ kJ mol}^{-1}}$$

3. $TcCl_6^{2-}$: *Hexachlorotechnetate Ion*

a. Recent Studies

i. *Structure*

$$K_2TcCl_6 \ (a_0 - 9.83 \text{ Å}, \ u = 0.2391) \ (20)$$

ii. *Charge distribution*

$$q_{Cl} = -0.49$$

iii. *Lattice energies.* Over the range $0.0 \geqslant q_{Cl} \geqslant -0.9$ [Eq. (38) has no roots at $q_{Cl} = -1.0$] we find that $U_{POT}(K_2TcCl_6)$ varies from 1322 kJ mol^{-1} to 1575 kJ mol^{-1} and the "basic" radius of the ion varies from 1.8 Å to 2.8 Å. At a charge distribution corresponding to $q_{Cl} = -0.49$, we find by interpolation:

$$U_{POT}(K_2TcCl_6) = 1443 \text{ kJ mol}^{-1}$$

iv. *"Basic" radius of ion*

$$\boxed{\bar{r}_{TcCl_6^{2-}} = 2.59 \text{ Å}}$$

No thermochemical data exist for these salts.

b. *Derived Estimates*

i. *Structures*

$$Rb_2TcCl_6 \ (a_0 = 9.965 \text{ Å}) \ (63)$$

ii. *Prediction of lattice energies*
Assigned value:

$$\boxed{U_{POT}(Rb_2TcCl_6) = 1417 \text{ kJ mol}^{-1}}$$

4. $ReCl_6^{2-}$: *Hexachlororhenate Ion*

a. Recent Studies

i. *Structure*

$$K_2ReCl_6 \ (a_0 = 9.84 \text{ Å}, u = 0.2391) \ (27)$$

ii. *Charge distribution*

$$q_{Cl} = -0.55$$

iii. *Lattice energies*

$$\boxed{U_{POT}(K_2ReCl_6) = 1416 \text{ kJ mol}^{-1}}$$

iv. "*Basic*" *radius of ion* (Fig. 18)

$$\boxed{\bar{r}_{ReCl_6^{2-}} = 2.54 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^\theta(K_2ReCl_6)(c) = -1333 \text{ kJ mol}^{-1} \ (56), \ -1331 \text{ kJ mol}^{-1} \ (10b);$$
$$\Delta H_f^\theta((NH_4)_2ReCl_6)(c) = -1056.5 \text{ kJ mol}^{-1} \ (23).$$

Assigned value:

$$\boxed{\Delta H_f^\theta(ReCl_6^{2-})(g) = -919 \pm 26 \text{ kJ mol}^{-1}}$$

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H_f^\theta(ReCl_6^{2-})(aq) = -761 \text{ kJ mol}^{-1} \ (56), \ -766 \text{ kJ mol}^{-1} \ (10b).$$

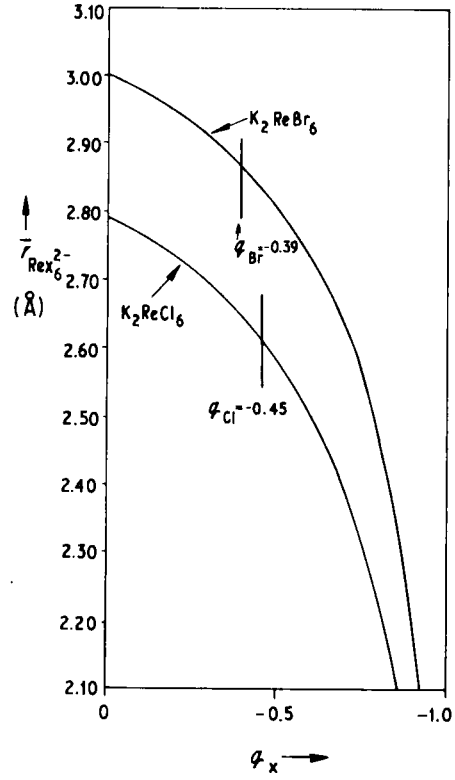


FIG. 18. Basic radii for the ions, $ReCl_6^{2-}$ and $ReBr_6^{2-}$, corresponding to lattice potential energy minima, as functions of charge distributions, q_X, on the halogen atom.

Assigned value

$$\boxed{\Delta H^{\theta}_{hyd}(ReCl_6^{2-})(g) = -709 \pm 26 \text{ kJ mol}^{-1}}$$

vii. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(ReCl_4)(c) = -361 \text{ kJ mol}^{-1} \ (57).$$

Assigned value:

$$\boxed{\overline{\Delta H}_{Cl(c)} = -66 \pm 26 \text{ kJ mol}^{-1}}$$

viii. *Prediction of lattice energies*
Ancillary data:

$$U_{POT}(K_2ReCl_6) = 1416 \text{ kJ mol}^{-1},$$

assuming

$$U_{POT}(K_2ReCl_6) \simeq U_{POT}((NH_4)_2ReCl_6).$$

Assigned value

$$\boxed{U_{POT}((NH_4)_2ReCl_6) \simeq 1416 \text{ kJ mol}^{-1}}$$

b. *Derived Estimates*

i. *Structures*

Rb_2ReCl_6 ($a_0 = 9.974$ Å) (*4*)
Cs_2ReCl_6 ($a_0 = 10.26$ Å) (*4*)
$(NH_4)_2ReCl_6$ ($a_0 = 9.98$ Å) (*13*)
$(NH_4)_2ReCl_6$ ($a_0 = 10.07$ Å) (*10*)

ii. *Prediction of lattice energies*

$$\boxed{\begin{aligned} U_{POT}(Rb_2ReCl_6) &= 1414 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2ReCl_6) &= 1398 \text{ kJ mol}^{-1} \\ U_{POT}((NH_4)_2ReCl_6) &= 1402 \text{ kJ mol}^{-1} \\ U_{POT}((NH_4)_2ReCl_6) &= 1374 \text{ kJ mol}^{-1} \end{aligned}}$$

c. *Previous Calculations.* Lister *et al.* (*53*) tabulated values of the lattice energy obtained for K_2ReCl_6 in 1974; these are listed in Table I. The values that should correspond most closely to those we obtain in this present study, in that they recognize a distributed charge on the $ReCl_6^{2-}$ ion, are the ones given in column e of Table I.

Burgess and Cartwright (*10a*) have obtained the enthalpy of solution of Cs_2ReCl_6 as $+88$ kJ mol^{-1} and obtain:

$$\Delta H^{\theta}_{hyd}(ReCl_6^{2-})(g) = -845 \text{ kJ mol}^{-1}$$

Busey, Dearman and Bevan (*10b*) have determined the enthalpy of solution of K_2ReCl_6 as $+43.5$ kJ mol^{-1} from which Burgess and Cartwright calculate:

$$\Delta H^{\theta}_{hyd}(ReCl_6{}^{2-})(g) = -827 \text{ kJ mol}^{-1}$$

A mean value:

$$\Delta H^{\theta}_{hyd}(ReCl_6{}^{2-})(g) = -836 \text{ kJ mol}^{-1}$$

is proposed. They use Kapustinskii's equation to obtain:

$$U_{POT}(Cs_2ReCl_6) = 1453 \text{ kJ mol}^{-1}$$
$$U_{POT}(K_2ReCl_6) = 1459 \text{ kJ mol}^{-1}$$

5. $ReBr_6{}^{2-}$: *Hexabromorhenate Ion*

a. Recent Calculations

i. *Structure*

$$K_2ReBr_6 \ (a_0 = 10.385 \text{ Å}, u = 0.2391) \ (27)$$

ii. *Charge distribution*

$$q_{Br} = -0.5$$

iii. *Lattice energies*

$$\boxed{U_{POT}(K_2ReBr_6) = 1375 \text{ kJ mol}^{-1}}$$

iv. "*Basic*" *radius of ion* (Fig. 18)

$$\boxed{\bar{r}_{ReBr_6{}^{2-}} = 2.81 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f{}^{\theta}(K_2ReBr_6)(c) = -1036 \text{ kJ mol}^{-1} \ (57).$$

Assigned value:

$$\boxed{\Delta H_f{}^{\theta}(ReBr_6{}^{2-})(g) = -689 \text{ kJ mol}^{-1}}$$

vi. *Halide ion affinities*

Ancillary data:

$$\Delta H_f^{\theta}(ReBr_4)(c) = -303 \text{ kJ mol}^{-1} \text{ (57)}.$$

Assigned value:

$$\boxed{\overline{\Delta H}_{Br(c)} = +82 \text{ kJ mol}^{-1}}$$

b. Previous Calculations. Burgess and Cartwright (*10a*) have assigned:

$$\Delta H_{hyd}^{\theta}(ReBr_6^{2-})(g) = -784 \text{ kJ mol}^{-1}$$

using lattice energies derived from Kapustinskii's equation giving:

$$U_{POT}(Cs_2ReBr_6) = 1399 \text{ kJ mol}^{-1}$$

F. Ruthenium(IV), Osmium(IV), Cobalt(IV), Iridium(IV), Nickel(IV), Palladium(IV), and Platinum(IV) Salts

1. $RuCl_6^{2-}$; *Hexachlororuthenate Ion*

a. Recent Studies. No crystal structure data are available.

b. Derived Estimates

i. *Structure*

$$K_2RuCl_6 \ (a_0 = 9.738 \text{ Å}) \text{ (74)}$$

ii. *Prediction of lattice energies*

$$\boxed{U_{POT}(K_2RuCl_6) = 1451 \text{ kJ mol}^{-1}}$$

2. $OsCl_6^{2-}$: *Hexachloroosmate Ion*

a. Recent Studies

i. *Structures*

$$K_2OsCl_6 \ (a_0 = 9.729 \text{ Å}, u = 0.243) \text{ (74)}$$

ii. *Charge distribution*

$$q_{Cl} = -0.51$$

iii. *Lattice energies*

$$U_{POT}(K_2OsCl_6) = 1447 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 19)

$$\bar{r}_{OsCl_6^{2-}} = 2.54 \text{ Å}$$

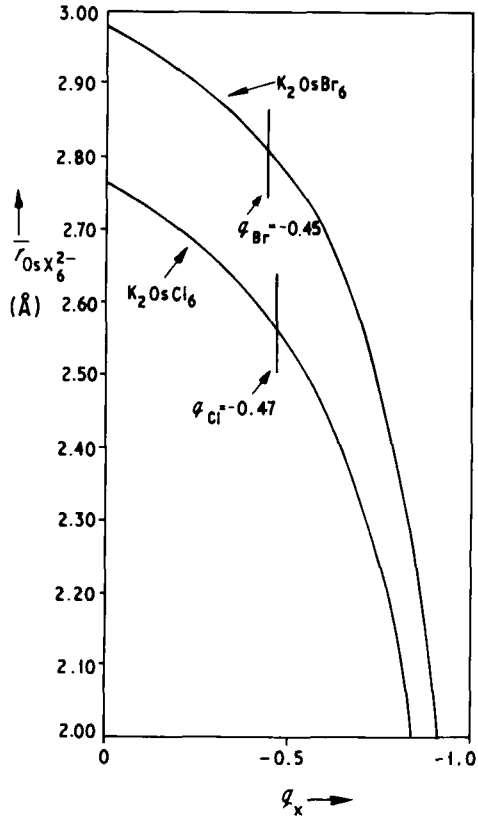


FIG. 19. Basic radius for the ions $OsCl_6^{2-}$ and $OsBr_6^{2-}$, corresponding to lattice energy minima, as functions of the charge, q_X, on the halogen atom.

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2OsCl_6)(c) = -1171 \text{ kJ mol}^{-1} \text{ (61)}$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(OsCl_6^{2-})(g) = -752 \text{ kJ mol}^{-1}}$$

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(OsCl_4)(c) = -255 \text{ kJ mol}^{-1} \text{ (56)}$$

and

$$\Delta H_f^{\theta}(OsCl_4)(g) = -79 \text{ kJ mol}^{-1} \text{ (56)}.$$

Assigned value:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(c)} &= -5 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -181 \text{ kJ mol}^{-1} \end{aligned}}$$

b. Derived Estimates

i. *Structures*

Cs_2OsCl_6 ($a_0 = 10.230$ Å) (*66*)

$(NH_4)_2OsCl_6$ ($a_0 = 9.881$ Å) (*67*)

ii. *Prediction of lattice energies*

$$\boxed{\begin{aligned} U_{POT}(Cs_2OsCl_6) &= 1409 \text{ kJ mol}^{-1} \\ U_{POT}((NH_4)_2OsCl_6) &= 1433 \text{ kJ mol}^{-1} \end{aligned}}$$

3. $OsBr_6^{2-}$: *Hexabromoosmate Ion*

a. Recent Studies

i. *Structures*

K_2OsBr_6 ($a_0 = 10.30$ Å, $u = 0.244$) (*74*)

ii. *Charge distribution*

$$q_{Br} = -0.45$$

iii. *Lattice energies*

$$\boxed{U_{POT}(K_2OsBr_6) = 1396 \text{ kJ mol}^{-1}}$$

iv. "*Basic*" *radius of ion* (Fig. 19)

$$\boxed{\bar{r}_{OsBr_6^{2-}} = 2.80 \text{ Å}}$$

No thermodynamic data exist for these salts.

4. CoF_6^{2-}: *Hexafluorocobaltate Ion*

a. Recent Studies

i. *Structures*

Rb_2CoF_6 ($a_0 = 8.46$ Å, $u = 0.2009$) (*60*)

Cs_2CoF_6 ($a_0 = 8.914$ Å, $u = 0.1907$) (*60*)

u was assigned on basis of Co–F ~ 1.7 Å as reported.

ii. *Charge distribution*

$$q_F = -0.59$$

iii. *Lattice energies*

$$U_{POT}(Rb_2CoF_6) = 1688 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2CoF_6) = 1632 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 20)

$$\boxed{\bar{r}_{CoF_6^{2-}} = 2.04 \text{ Å}}$$

No thermodynamic data exist for these salts.

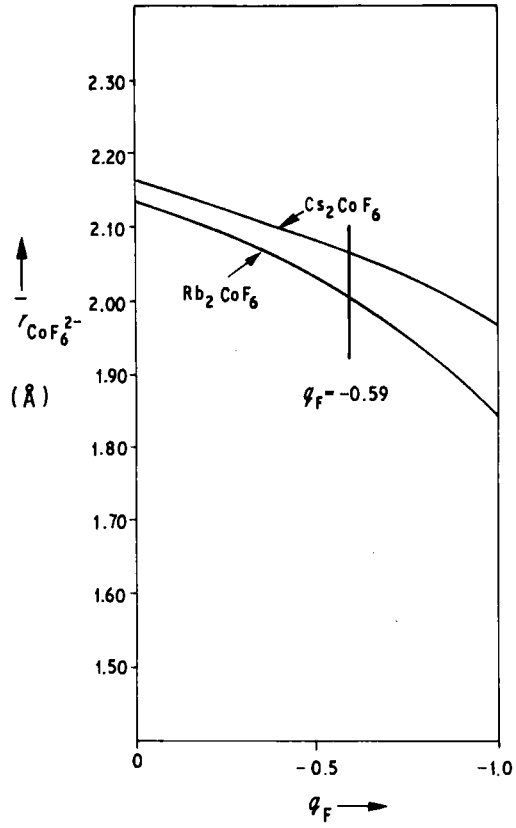


FIG. 20. Basic radius of CoF_6^{2-} ion, corresponding to lattice potential energy minima, as a function of q_F, the charge on the fluorine atoms.

5. $IrCl_6^{2-}$: *Hexachloroiridate Ion*

a. Recent Studies

i. *Structures*

$(NH_4)_2IrCl_6$ ($a_0 = 9.87$ Å, $u = 0.25$) (*74*)

ii. *Charge distribution*

$$q_{Cl} = -0.47$$

iii. *Lattice energies*

$$U_{POT}((NH_4)_2IrCl_6) = 1442 \text{ kJ mol}^{-1}$$

iv. *"Basic" radius of ion*

$$\boxed{\bar{r}_{IrCl_6^{2-}} = 2.56 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^\theta(K_2IrCl_6)(c) = -1197 \text{ kJ mol}^{-1} \text{ (61)}, \ -1176 \text{ kJ mol}^{-1} \text{ (68a)}$$

assuming that

$$U_{POT}(K_2IrCl_6) \simeq U_{POT}((NH_4)_2IrCl_6), \Delta H_f^\theta(Rb_2IrCl_6)(c)$$
$$= -1180 \text{ kJ mol}^{-1} \text{ (68a)}.$$

Assigned value:

$$\boxed{\Delta H_f^\theta(IrCl_6^{2-})(g) \sim -785 \text{ kJ mol}^{-1}}$$

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H_f^\theta(IrCl_6^{2-})(aq) = -619.7 \text{ kK mol}^{-1} \text{ (61)}.$$

Assigned value:

$$\boxed{\Delta H_{hyd}^\theta(IrCl_6^{2-})(g) = -706 \text{ kJ mol}^{-1}}$$

vii. *Prediction of lattice energies*
Ancillary data:

$$U_{POT}(K_2IrCl_6) \approx U_{POT}((NH_4)_2IrCl_6).$$

Assigned value:

$$\boxed{U_{POT}(K_2IrCl_6) \simeq 1442 \text{ kJ mol}^{-1}}$$

b. Previous Calculations. Burgess and Cartwright (*10a*) have estimated:

$$\Delta H_{hyd}^\theta(IrCl_6^{2-})(g) = -834 \text{ kJ mol}^{-1}$$

from a lattice energy:

$$U_{POT}((NH_4)_2IrCl_6) = 1505 \text{ kJ mol}^{-1}$$

6. NiF_6^{2-}: *Hexafluoronickalate Ion*

a. Recent Studies

i. *Structures*

K_2NiF_6 ($a_0 = 8.1088$ Å, $u = 0.219$) (*74*)

Rb_2NiF_6 ($a_0 = 8.462$ Å, $u = 0.202$) (*74*)

ii. *Charge distribution*

$$q_F = -0.57$$

iii. *Lattice energies*

$$\boxed{\begin{aligned} U_{POT}(K_2NiF_6) &= 1721 \text{ kJ mol}^{-1} \\ U_{POT}(Rb_2NiF_6) &= 1688 \text{ kJ mol}^{-1} \end{aligned}}$$

iv. "*Basic*" *radius of ion* (Fig. 21)

$$\boxed{\bar{r}_{NiF_6^{2-}} = 1.97 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2NiF_6)(c) = -2021 \pm 12 \text{ kJ mol}^{-1} \text{ (}32a\text{)}.$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(NiF_6^{2-})(g) = -1328 \pm 12 \text{ kJ mol}^{-1}}$$

7. $PdCl_6^{2-}$: *Hexachloropalladate Ion*

a. Recent Studies

i. *Structures*

$(NH_4)_2PdCl_6$ ($a_0 = 9.84$ Å, $u = 0.2337$) (*3*)

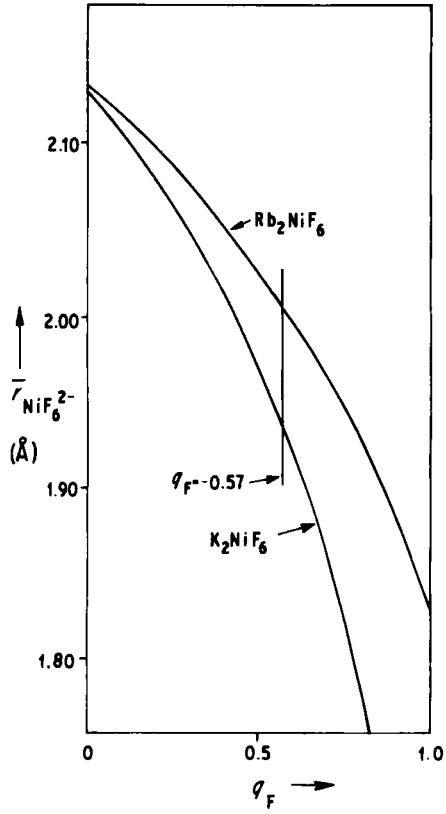


FIG. 21. Basic radius of the ion NiF_6^{2-}, corresponding to a lattice potential energy minima, as a function of the charge, q_F, on the fluorine atoms.

ii. *Charge distribution*

$$q_{Cl} = -0.43$$

iii. *Lattice energies*

$$U_{POT}[(NH_4)_2PdCl_6] = 1481 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion*

$$\bar{r}_{PdCl_6^{2-}} = 2.61 \text{ Å}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2PdCl_6)(c) = -1187 \text{ kJ mol}^{-1} \text{ (61)}$$

and assuming

$$U_{POT}(K_2PdCl_6) \approx U_{POT}((NH_4)_2PdCl_6).$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(PdCl_6^{2-})(g) = -734 \text{ kJ mol}^{-1}}$$

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(PdCl_6^{2-})(aq) = -598 \text{ kJ mol}^{-1} \text{ (56)}.$$

Assigned value:

$$\boxed{\Delta H_{hyd}^{\theta}(PdCl_6^{2-})(g) = -735 \text{ kJ mol}^{-1}}$$

b. Derived Estimates
i. *Structures*

K_2PdCl_6 (a_0 = 9.74 Å) (*74*)
Rb_2PdCl_6 (a_0 = 9.87 Å) (*74*)
Cs_2PdCl_6 (a_0 = 10.18 Å) (*74*)

ii. *Prediction of lattice energies*

$$\boxed{\begin{aligned} U_{POT}(K_2PdCl_6) &= 1450 \text{ kJ mol}^{-1} \\ U_{POT}(Rb_2PdCl_6) &= 1449 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2PdCl_6) &= 1426 \text{ kJ mol}^{-1} \end{aligned}}$$

iii. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2PdCl_6)(c) = -1187 \text{ kJ mol}^{-1} \text{ (61)}.$$

Assigned value:

$$\Delta H_f^{\theta}(PdCl_6^{2-})(g) = -765 \text{ kJ mol}^{-1}$$

c. Previous Calculations. Hartley (*29*) has used both the Born–Mayer (*6*) equation and the Kapustinskii (*46*) equation to estimate the lattice energy of K_2PdCl_6; his results are given in Table I.

8. $PtCl_6^{2-}$: *Hexachloroplatinate Ion*

a. Recent Studies

i. *Structures*

K_2PtCl_6 ($a_0 = 9.755$ Å, $u = 0.24$) (*74*)

Rb_2PtCl_6 ($a_0 = 9.901$ Å, $u = 0.235$) (*74*)

Cs_2PtCl_6 ($a_0 = 10.215$ Å, $u = 0.23$) (*74*)

$(NH_4)_2PtCl_6$ ($a_0 = 9.858$ Å, $u = 0.24$) (*74*)

Tl_2PtCl_6 ($a_0 = 9.799$ Å, $u = 0.235$) (*74*)

ii. *Charge distribution*

$$q_{Cl} = -0.44$$

iii. *Lattice energies*

$$U_{POT}(K_2PtCl_6) = 1468 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2PtCl_6) = 1464 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2PtCl_6) = 1444 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2PtCl_6) = 1468 \text{ kJ mol}^{-1}$$
$$U_{POT}(Tl_2PtCl_6) = 1546 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 22)

$$\bar{r}_{PtCl_6^{2-}} = 2.59 \text{ Å}$$

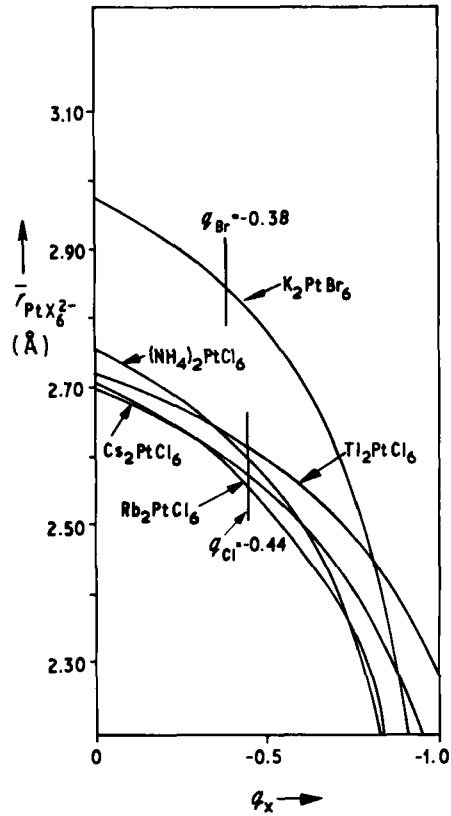


FIG. 22. Basic radii of the ions, $PtCl_6^{2-}$ and $PtBr_6^{2-}$, corresponding to lattice energy minima, as functions of the charge, q_X, on the halogen atoms.

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(PtCl_6^{2-})(aq) = -678 \pm 4 \text{ kJ mol}^{-1} \text{ (24)}$$

$$\Delta H_f^{\theta}(K_2PtCl_6)(c) = -1235 \text{ kJ mol}^{-1} \text{ (68a)}, \Delta H_f^{\theta}(Rb_2PtCl_6)(c) = -1251 \text{ kJ mol}^{-1} \text{ (68a)}$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(PtCl_6^{2-})(g) = -792 \text{ kJ mol}^{-1}}$$

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H^{\theta}_{soln}(K_2PtCl_6)(c) = 56.5 \text{ kJ mol}^{-1} \text{ (14)}$$

and

$$\Delta H^{\theta}_{soln}((NH_4)_2PtCl_6)(c) = 49.8 \text{ kJ mol}^{-1} \text{ (65)}$$

Assigned value:

$$\boxed{\Delta H^{\theta}_{hyd}(PtCl_6^{2-})(g) = -757 \pm 6 \text{ kJ mol}^{-1}}$$

vii. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(PtCl_4)(c) = -263.2 \text{ kJ mol}^{-1} \text{ (56)}$$

Assigned value:

$$\boxed{\overline{\Delta H}_{Cl(c)} = -37 \text{ kJ mol}^{-1}}$$

viii. *Prediction of lattice energies*
Ancillary data:

$$\Delta H_f^{\theta}(Ag_2PtCl_6)(c) = -527 \text{ kJ mol}^{-1} \text{ (24)},$$
$$\Delta H_f^{\theta}(BaPtCl_6)(c) = -1180 \text{ kJ mol}^{-1} \text{ (24)}.$$

Assigned value:

$$\boxed{\begin{aligned} U_{POT}(Ag_2PtCl_6) &= 1773 \text{ kJ mol}^{-1} \\ U_{POT}(BaPtCl_6) &= 2047 \text{ kJ mol}^{-1} \end{aligned}}$$

c. Previous Calculations. Hartley (*29*), Lister *et al.* (*53*), DeJonge (*16*), and Jenkins (*36*) have all studied the lattice potential energies. All the approaches used have differed from the present one and, aside from the simple Born–Lande approach of Lister *et al.* (*53*), only the calculated value of Jenkins approaches the present value. The results are tabulated in Table I.

Burgess and Cartwright (*10a*) have estimated:

$$U_{POT}(K_2PtCl_6) = 1521 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2PtCl_6) = 1459 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2PtCl_6) = 1507 \text{ kJ mol}^{-1}$$

leading to:

$$\Delta H^{\theta}_{hyd}(PtCl_6^{2-})(g) = -844 \text{ kJ mol}^{-1}$$

9. $PtBr_6^{2-}$: *Hexabromoplatinate Ion*

a. Recent Studies

i. *Structures*

K_2PtBr_6 ($a_0 = 10.293$ Å, $u = 0.2391$) (*3*)

ii. *Charge distribution*

$$q_{Br} = -0.38$$

iii. *Lattice energies*

$$\boxed{U_{POT}(K_2PtBr_6) = 1423 \text{ kJ mol}^{-1}}$$

iv. "*Basic*" *radius of ion* (Fig. 22)

$$\boxed{\bar{r}_{PtBr_6^{2-}} = 2.85 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2PtBr_6)(c) = -1040 \text{ kJ mol}^{-1} \text{ (}61\text{)}.$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(PtBr_6^{2-})(g) = -645 \text{ kJ mol}^{-1}}$$

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(PtBr_6^{2-})(aq) = -477 \text{ kJ mol}^{-1} (56).$$

Assigned value:

$$\boxed{\Delta H_{hyd}^{\theta}(PtBr_6^{2-})(g) = -703 \text{ kJ mol}^{-1}}$$

vii. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(PtBr_4)(c) = -159 \text{ kJ mol}^{-1} (56).$$

Assigned value:

$$\boxed{\Delta H_{Br(c)} = -18 \text{ kJ mol}^{-1}}$$

viii. *Prediction of lattice energies*
Ancillary data:

$$\Delta H_f^{\theta}(Ag_2PtBr_6)(c) = -398 \text{ kJ mol}^{-1} (56).$$

Assigned value:

$$\boxed{U_{POT}(Ag_2PtBr_6) = 1791 \text{ kJ mol}^{-1}}$$

c. Previous Calculations. Hartley (*29*), Lister *et al.* (*53*), and DeJonge (*16*) have all calculated the lattice energy of K_2PtBr_6, and the results are given in Table I. Hartley (*29*) and DeJonge (*16*) have estimated the Pt—Br bond strength.

Burgess and Cartwright (*10a*) have calculated:

$$U_{POT}(K_2PtBr_6) = 1451 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2PtBr_6) = 1439 \text{ kJ mol}^{-1}$$

from which they estimate:

$$\Delta H_{hyd}^{\theta}(PtBr_6^{2-})(g) = -769 \text{ kJ mol}^{-1}$$

G. Silicon(IV), Germanium(IV), Tin(IV), and Lead(IV) Salts

1. SiF_6^{2-}: *Hexafluorosilicate Ion*

a. *Recent Studies*

i. *Structures*

K_2SiF_6 ($a_0 = 8.133$ Å, $u = 0.215$) (*74*)

Rb_2SiF_6 ($a_0 = 8.452$ Å, $u = 0.20$) (*74*)

Cs_2SiF_6 ($a_0 = 8.919$ Å, $u = 0.19$) (*74*)

Tl_2SiF_6 ($a_0 = 8.568$ Å, $u = 0.20$) (*74*)

$(NH_4)_2SiF_6$ ($a_0 = 8.395$ Å, $u = 0.205$) or ($a_0 = 8.395$ Å, $u = 0.2011$) (*28, 62*)

ii. *Charge distribution*

$$q_F = -0.84$$

iii. *Lattice energies*

$$U_{POT}(K_2SiF_6) = 1670 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2SiF_6) = 1639 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2SiF_6) = 1604 \text{ kJ mol}^{-1}$$
$$U_{POT}(Tl_2SiF_6) = 1675 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2SiF_6) = 1657 \text{ kJ mol}^{-1} \text{ or } 1665 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 23)

$$\bar{r}_{SiF_6^{2-}} = 1.94 \text{ Å}$$

v. *Enthalpy of formation of gaseous ion* (Fig. 24)
Ancillary data:

$$\Delta H_f^\theta(K_2SiF_6)(c) = -2807 \text{ kJ mol}^{-1} (61), \; -2966 \text{ kJ mol}^{-1} (68a)$$
$$\Delta H_f^\theta(Rb_2SiF_6)(c) = -2838 \text{ kJ mol}^{-1} (61), \; -2911.6 \text{ kJ mol}^{-1} (68a)$$
$$\Delta H_f^\theta(Cs_2SiF_6)(c) = -2801 \text{ kJ mol}^{-1} (61),$$
$$\Delta H_f^\theta((NH_4)_2SiF_6)(c) = -2681 \text{ kJ mol}^{-1} (56).$$

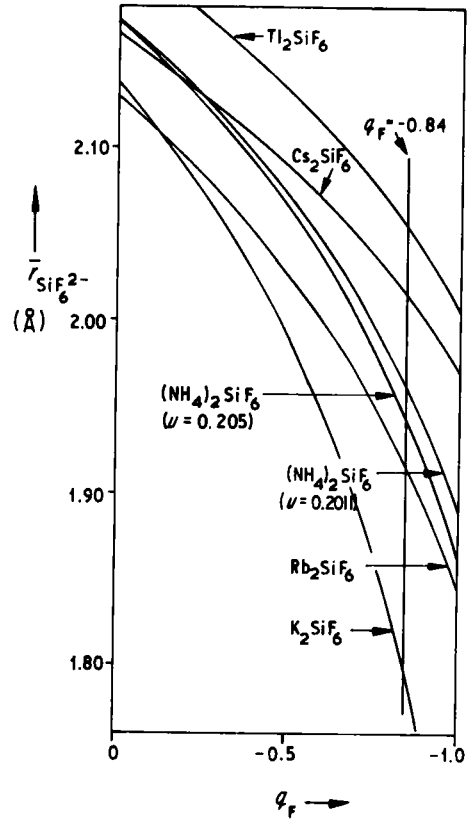


FIG. 23. Basic radius of the ion, SiF_6^{2-}, corresponding to lattice potential energy minima, as a function of the charge distribution, q_F, on the fluorine atom.

Assigned value:

$$\boxed{\Delta H_f^\theta(SiF_6^{2-})(g) = -2198 \pm 75 \text{ kJ mol}^{-1}*}$$

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H_f^\theta(SiF_6^{2-})(aq) = -2389 \text{ kJ mol}^{-1} (56).$$

* Assigned in noncubic salt calculations also (Ref. 40a).

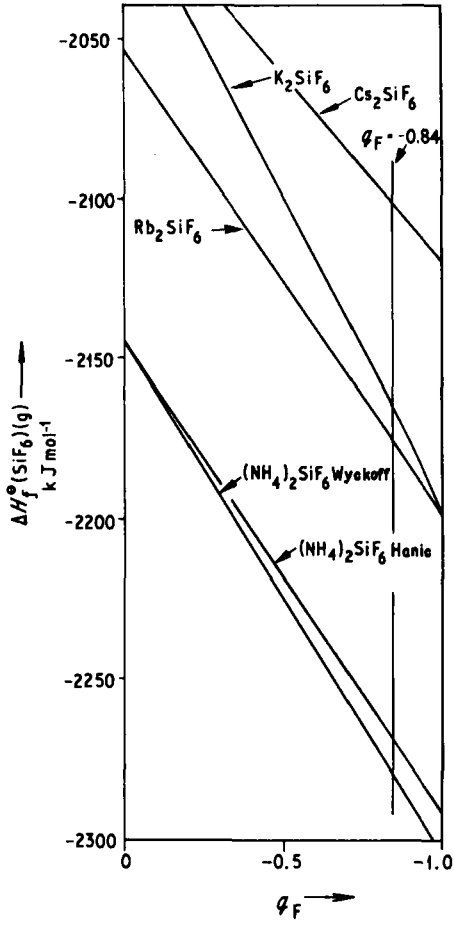


FIG. 24. Enthalpy of formation, $\Delta H_f^\theta(SiF_6^{2-})(g)$, corresponding to lattice potential energy minima, as a function of the charge distribution q_F, on the fluorine atom.

Assigned value:

$$\Delta H^\theta_{hyd}(SiF_6^{2-})(g) = -1071 \pm 75 \text{ kJ mol}^{-1}$$

vii. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^\theta(SiF_4)(g) = -1615 \text{ kJ mol}^{-1} \text{ (56)}.$$

Assigned value:

$$\boxed{\overline{\Delta H}_{F(g)} = -42 \pm 75 \text{ kJ mol}^{-1}*}$$

2. GeF_6^{2-}: *Hexafluorogermanate ion*

a. Recent Studies

i. *Structures*

Cs_2GeF_6 ($a_0 = 9.021$ Å, $u = 0.20$) (*74*)

$(NH_4)_2GeF_6$ ($a_0 = 8.46$ Å, $u = 0.203$) (*74*)

ii. *Charge distribution*

$$q_F = -0.78$$

iii. *Lattice energies*

$$\boxed{\begin{aligned} U_{POT}(Cs_2GeF_6) &= 1573 \text{ kJ mol}^{-1} \\ U_{POT}((NH_4)_2GeF_6) &= 1657 \text{ kJ mol}^{-1} \end{aligned}}$$

iv. "*Basic*" *radius of ion* (Fig. 25)

$$\boxed{\bar{r}_{GeF_6^{2-}} = 2.01 \text{ Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$U_{POT}[(NH_4)_2GeF_6] \simeq U_{POT}(K_2GeF_6);$$
$$\Delta H_f^{\theta}(K_2GeF_6)(c) = -2600 \pm 8 \text{ kJ mol}^{-1} \text{ (32a)}.$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(GeF_6^{2-})(g) = -1971 \text{ kJ mol}^{-1}}$$

* Assigned in noncubic salt calculations also (Ref. 40a).

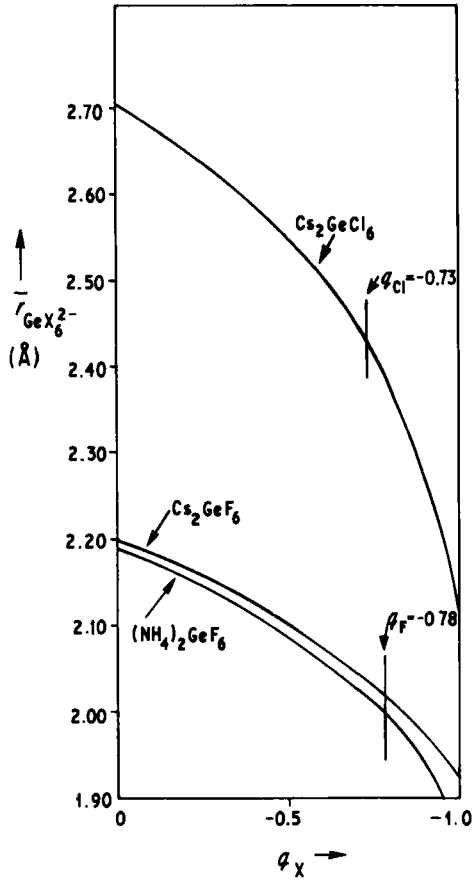


FIG. 25. Basic radii of the ions GeF_6^{2-} and $GeCl_6^{2-}$ corresponding to lattice potential energy minima, as a function of the charge, q_X on the halogen atom.

vi. *Halide Ion Affinity:*
Ancillary Data:

$$\Delta H_f^{\theta}(GeF_4)(g) = -1190 \text{ kJ mol}^{-1} \quad (26a)$$

Assigned value:

$$\boxed{\overline{\Delta H}_{F(g)} = -240 \text{ kJ mol}^{-1}}$$

3. $GeCl_6^{2-}$: *Hexachlorogermanate ion*

a. Recent Studies

i. *Structures*

$$Cs_2GeCl_6\ (a_0 = 10.21\ \text{Å},\ u = 0.23)\ (74)$$

ii. *Charge distribution*

$$q_{Cl} = -0.73$$

iii. *Lattice energies*

$$\boxed{U_{POT}(Cs_2GeCl_6) = 1375\ \text{kJ mol}^{-1}}$$

iv. *"Basic" radius of ion* (Fig. 25)

$$\boxed{\bar{r}_{GeCl_6^{2-}} = 2.43\ \text{Å}}$$

v. *Enthalpy of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(Rb_2GeCl_6)(c) = -1464\ \text{kJ mol}^{-1}\ (68a)$$
$$\Delta H_f^{\theta}(Cs_2GeCl_6)(c) = -1451.8\ \text{kJ mol}^{-1}\ (70).$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(GeCl_6^{2-})(g) = -981\ \text{kJ mol}^{-1}}$$

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(GeCl_4)(l) = -532\ \text{kJ mol}^{-1}\ (56),$$
$$\Delta H_f^{\theta}(GeCl_4)(g) = -496\ \text{kJ mol}^{-1}\ (56).$$

Assigned values:

$$\boxed{\begin{aligned}\overline{\Delta H}_{Cl(l)} &= +43\ \text{kJ mol}^{-1}\\ \overline{\Delta H}_{Cl(g)} &= +7\ \text{kJ mol}^{-1}\end{aligned}}$$

c. Previous Calculations. Welsh *et al.* (*70*) have calculated the lattice energy of Cs_2GeCl_6 using Wood's method (*2*, *18*, *21*, *72*, *73*). They obtained the results given in Table I together with the following thermochemical data:

$$\Delta H_f^{\theta}(GeCl_6^{2-})(g) = -956 \pm 84 \text{ kJ mol}^{-1}$$

$$\overline{\Delta H}_{Cl(g)} = +32 \pm 84 \text{ kJ mol}^{-1}$$

this latter term being referred to as the donor–acceptor bond energy, aside from a sign reversal.

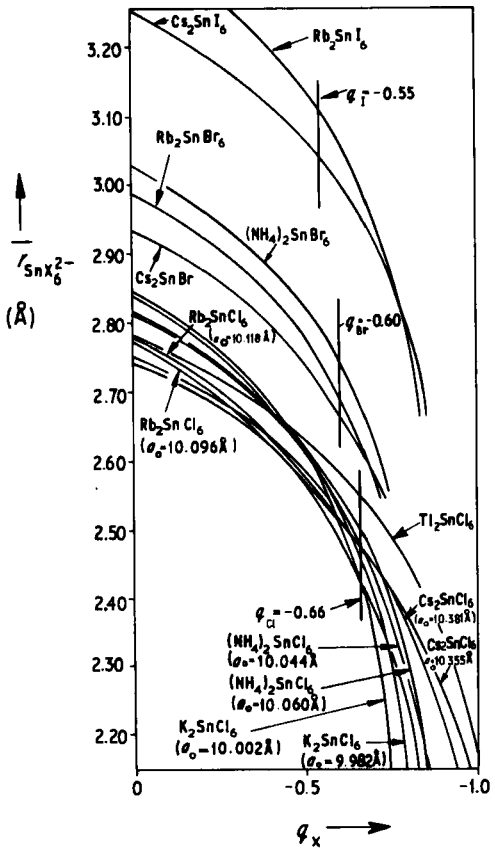


FIG. 26. Basic radii for ions $SnCl_6^{2-}$, $SnBr_6^{2-}$, and SnI_6^{2-}, corresponding to lattice potential energy minima, as a function of the charge distributions, q_X, on the halogen atoms.

4. $SnCl_6^{2-}$: *Hexachlorostannate Ion*

a. Recent Studies

i. *Structures*

K_2SnCl_6 ($a_0 = 10.002$ Å, $u = 0.245$) (*74*) or ($a_0 = 9.982$ Å, $u = 0.2415$) (*7*)

Rb_2SnCl_6 ($a_0 = 10.118$ Å, $u = 0.24$) (*74*) or ($a_0 = 10.096$ Å, $u = 0.2399$) (*7*)

Cs_2SnCl_6 ($a_0 = 10.381$ Å, $u = 0.235$) (*74*) or ($a_0 = 10.355$ Å, $u = 0.234$) (*7*)

Tl_2SnCl_6 ($a_0 = 9.97$ Å, $u = 0.24$) (*74*)

$(NH_4)_2SnCl_6$ ($a_0 = 10.060$ Å, $u = 0.24$) (*74*) or ($a_0 = 10.044$ Å, $u = 0.2411$) (*7*)

Recently Lerbscher and Trotter have redetermined the structure of

$$K_2SnCl_6 (a_0 = 9.990 \text{ Å}, u = 0.2411) (52a)$$

$$(NH_4)_2SnCl_6 (a_0 = 10.038 \text{ Å}, u = 0.2412) (52a)$$

these are very similar to the structures of reference (*7*).

ii. *Charge distribution*

$$q_{Cl} = -0.66$$

iii. *Lattice energies*

$$U_{POT}(K_2SnCl_6) = 1352 \text{ kJ mol}^{-1} \text{ or } 1363 \text{ kJ mol}^{-1}$$
$$U_{POT}(Rb_2SnCl_6) = 1358 \text{ kJ mol}^{-1} \text{ or } 1361 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2SnCl_6) = 1352 \text{ kJ mol}^{-1} \text{ or } 1358 \text{ kJ mol}^{-1}$$
$$U_{POT}(Tl_2SnCl_6) = 1437 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2SnCl_6) = 1369 \text{ kJ mol}^{-1} \text{ or } 1370 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 26)

$$\bar{r}_{SnCl_6^{2-}} = 2.47 \text{ Å}$$

v. *Enthalpy of formation of gaseous ion* (Fig. 27)
Ancillary data:

$\Delta H_f^{\theta}(K_2SnCl_6)(c) = -1518$ kJ mol^{-1} (*61*), -1485 kJ mol^{-1} (*70*), -1481.7 kJ mol^{-1} (*62a*);

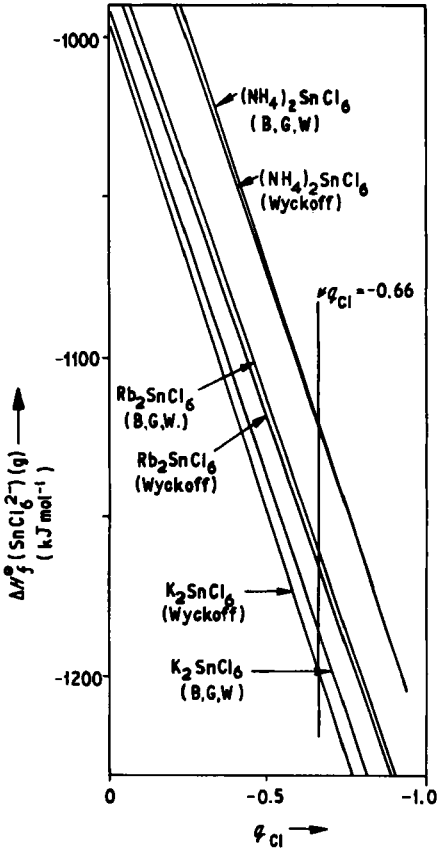


FIG. 27. Enthalpy of formation, $\Delta H_f^\theta(SnCl_6^{2-})(g)$, corresponding to a lattice potential energy minimum, as a function of the charge, q_{Cl}, on the chlorine atom.

$\Delta H_f^\theta(Rb_2SnCl_6)(c) = -1529$ kJ mol^{-1} (*69*);
$\Delta H_f^\theta[(NH_4)_2SnCl_6)(c) = -1237$ kJ mol^{-1} (*56*),
-1281 ± 17 kJ mol^{-1} (*64a*)*, -1244.1 kJ mol^{-1} (*10a*).

Assigned value:

$$\Delta H_f^\theta(SnCl_6^{2-})(g) = -1156 \pm 27 \text{ kJ mol}^{-1}$$

* This value has not been used for the analysis in Fig. 27, but clearly to do so would improve the agreement.

vi. *Enthalpy of hydration of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(SnCl_6^{2-})(aq) = -970 \text{ kJ mol}^{-1} \text{ (56)}.$$

Assigned value:

$$\boxed{\Delta H_{hyd}^{\theta}(SnCl_6^{2-})(aq) = -685 \pm 27 \text{ kJ mol}^{-1}}$$

vii. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(SnCl_4)(l) = -511 \text{ kJ mol}^{-1} \text{ (56)}. \; -520 \text{ kJ mol}^{-1} \text{ (54b)}$$

and

$$\Delta H_f^{\theta}(SnCl_4)(g) = -472 \text{ kJ mol}^{-1} \text{ (56)},$$

Assigned value:

$$\boxed{\begin{aligned} \overline{\Delta H}_{Cl(l)} &= -153 \pm 27 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -192 \pm 27 \text{ kJ mol}^{-1} \end{aligned}}$$

c. Previous Calculations. Webster and Collins (*69*), Lister *et al.* (*53*), Welsh *et al.* (*70*), Gelbman and Westland (*22*), and Jenkins and Smith (*40*) have all made studies of the lattice energies of hexachlorostannate salts, the results are compared in Table I. The following thermodynamic estimates were obtained from the studies:
Webster and Collins (*69*):

$$\begin{aligned} \overline{\Delta H}_{Cl(g)} &= -90.8 \pm 71 \text{ kJ mol}^{-1} \\ \Delta H_f^{\theta}(SnCl_6^{2-})(g) &= -1070 \pm 71 \text{ kJ mol}^{-1} \end{aligned}$$

Welsh *et al.* (*70*):

$$\begin{aligned} \Delta H_f^{\theta}(SnCl_6^{2-})(g) &= -1125 \pm 84 \text{ kJ mol}^{-1} \\ \overline{\Delta H}_{Cl(g)} &= -161 \pm 84 \text{ kJ mol}^{-1} \end{aligned}$$

Gelbman and Westland (*22*):

$$U_{POT}(K_2SnCl_6) - U_{POT}(K_2ZrCl_6) \simeq 15 \text{ kJ mol}^{-1} \quad (77)$$

and following the work of Brill *et al.* (*7*), they obtain

$$\overline{\Delta H}_{Cl(g)} = -1547 + U_{POT}(K_2SnCl_6) \text{ kJ mol}^{-1} \quad (78)$$

which when used in conjunction with their cited lattice energies (see Section V,B,3,c) give

$$U_{POT}(K_2ZrCl_6) = 1571 \text{ kJ mol}^{-1}$$

whereupon

$$U_{POT}(K_2SnCl_6) = 1586 \text{ kJ mol}^{-1}$$

which leads to

$$\overline{\Delta H}_{Cl(g)} = +39 \text{ kJ mol}^{-1}$$

Jenkins and Smith (*40*)

$$\Delta H_f^{\theta}(SnCl_6^{2-})(g) = -1256 \text{ kJ mol}^{-1}$$
$$\overline{\Delta H}_{Cl(g)} = -278 \text{ kJ mol}^{-1}$$

5. $SnBr_6^{2-}$: *Hexabromostannate Ion*

a. Recent Studies

i. *Structures*

Rb_2SnBr_6 ($a_0 = 10.64$ Å, $u = 0.245$) (*74*)

Cs_2SnBr_6 ($a_0 = 10.81$ Å, $u = 0.245$) (*74*)

$(NH_4)_2SnBr_6$ ($a_0 = 10.59$ Å, $u = 0.245$) (*74*)

ii. *Charge distribution*

$$q_{Br} = -0.60$$

iii. *Lattice energies*

$$U_{POT}(Rb_2SnBr_6) = 1309 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2SnBr_6) = 1306 \text{ kJ mol}^{-1}$$
$$U_{POT}[(NH_4)_2SnBr_6] = 1319 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 26)

$$\bar{r}_{SnBr_6^{2-}} = 2.70 \text{ Å}$$

No thermochemical data exist for these salts.

c. Previous Calculations. Makhija and Westland (*54a*) have cited the relationship:

$$\overline{\Delta H}_{Br(g)} = -1459 + U_{pot}(K_2SnBr_6) \text{ kJ mol}^{-1} \tag{79}$$

and employing their lattice energies as given in Table I they find:

$$\overline{\Delta H}_{Br(g)} = +46 \text{ kJ mol}^{-1}$$

6. SnI_6^{2-}: *Hexaiodostannate Ion*

a. Recent Studies

i. *Structures*

Rb_2SnI_6 ($a_0 = 11.60$ Å, $u = 0.245$) (*74*)

Cs_2SnI_6 ($a_0 = 11.63$ Å, $u = 0.245$) (*74*)

ii. *Charge distribution*

$$q_I = -0.55$$

iii. *Lattice energies*

$$U_{POT}(Rb_2SnI_6) = 1226 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2SnI_6) = 1243 \text{ kJ mol}^{-1}$$

iv. *"Basic" radius of ion* (Fig. 26)

$$\boxed{\bar{r}_{SnI_6^{2-}} = 3.07 \text{ Å}}$$

No thermochemical data exist for these salts.

7. $PbCl_6^{2-}$: *Hexachloroplumbate Ion*

a. Previous Studies

i. *Structures*

Rb_2PbCl_6 ($a_0 = 10.197$ Å, $u = 0.2445$) (*74*)

Cs_2PbCl_6 ($a_0 = 10.415$ Å, $u = 0.24$) (*74*)

$(NH_4)_2PbCl_6$ ($a_0 = 10.135$ Å, $u = 0.245$) (*74*)

ii. *Charge distribution*

$$q_{Cl} = -0.63$$

iii. *Lattice energies*

$$\boxed{\begin{aligned} U_{POT}(Rb_2PbCl_6) &= 1343 \text{ kJ mol}^{-1} \\ U_{POT}(Cs_2PbCl_6) &= 1344 \text{ kJ mol}^{-1} \\ U_{POT}[(NH_4)_2PbCl_6] &= 1355 \text{ kJ mol}^{-1} \end{aligned}}$$

iv. *"Basic" radius of ion* (Fig. 28)

$$\boxed{\bar{r}_{PbCl_6^{2-}} = 2.48 \text{ Å}}$$

v. *Enthalpy of formation of the gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(Rb_2PbCl_6)(c) = -1293 \text{ kJ mol}^{-1} \text{ (70)}.$$

Assigned value:

$$\boxed{\Delta H_f^{\theta}(PbCl_6^{2-})(g) = -940 \text{ kJ mol}^{-1}}$$

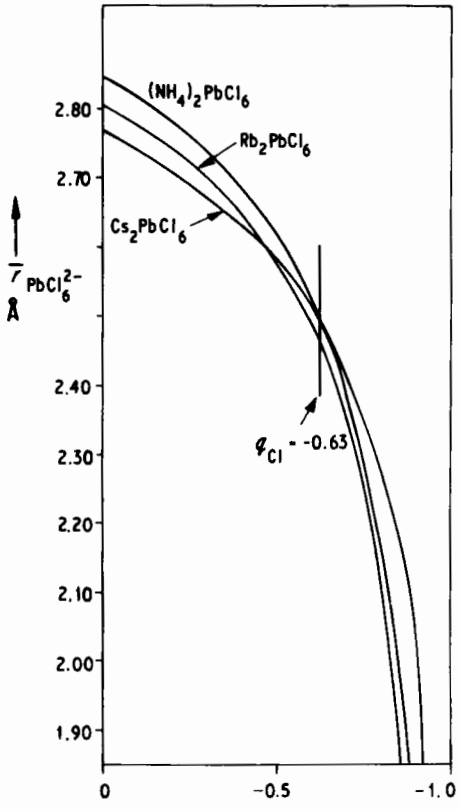


FIG. 28. Basic radius for the $PbCl_6^{2-}$ ion, corresponding to a lattice potential energy minimum, as a function of the charge distribution, q_{Cl}, on the halogen atom.

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(PbCl_4)(l) = -329 \text{ kJ mol}^{-1} \text{ (56)},$$
$$\Delta H_f^{\theta}(PbCl_4)(g) = -285 \pm 8 \text{ kJ mol}^{-1} \text{ (70)}.$$

Assigned value:

$$\overline{\Delta H}_{Cl(l)} = -119 \text{ kJ mol}^{-1}$$
$$\overline{\Delta H}_{Cl(g)} = -163 \pm 8 \text{ kJ mol}^{-1}$$

b. Previous Calculations. Welsh *et al.* (*70*) have calculated the lattice energy of Rb_2PbCl_6 (Table I). The associated thermochemical data derived assigned:

$$\Delta H_f^{\theta}(PbCl_6^{2-})(g) = -927 \pm 92 \text{ kJ mol}^{-1}$$

$$\overline{\Delta H}_{Cl(g)} = -150 \pm 92 \text{ kJ mol}^{-1}$$

H. ANTIMONY(IV) SALTS

1. $SbCl_6^{2-}$: *Hexachloroantimonate Ion*

a. Recent Calculations. No crystal structure data are available.

b. Derived Values

i. *Structure*

$$Rb_2SbCl_6 \ (a_0 = 10.14 \text{ Å}) \ (41)$$

ii. *Prediction of lattice energy*

$$U_{POT}(Rb_2SbCl_6) = 1357 \text{ kJ mol}^{-1}$$

I. SELENIUM(IV), TELLURIUM(IV), AND POLONIUM(IV) SALTS

1. $SeCl_6^{2-}$: *Hexachloroselenate Ion*

a. Recent Studies

i. *Structures*

$$Rb_2SeCl_6 \ (a_0 = 9.978 \text{ Å}, u = 0.24) \ (74)$$

$$Cs_2SeCl_6 \ (a_0 = 10.266 \text{ Å}, u = 0.235) \ (74)$$

$$(NH_4)_2SeCl_6 \ (a_0 = 9.935 \text{ Å}, u = 0.24) \ (74)$$

ii. *Charge distribution*

$$q_{Cl} = -0.56$$

iii. *Lattice energies*

$$U_{POT}(Rb_2SeCl_6) = 1409 \text{ kJ mol}^{-1}$$

$$U_{POT}(Cs_2SeCl_6) = 1397 \text{ kJ mol}^{-1}$$

$$U_{POT}[(NH_4)_2SeCl_6] = 1420 \text{ kJ mol}^{-1}$$

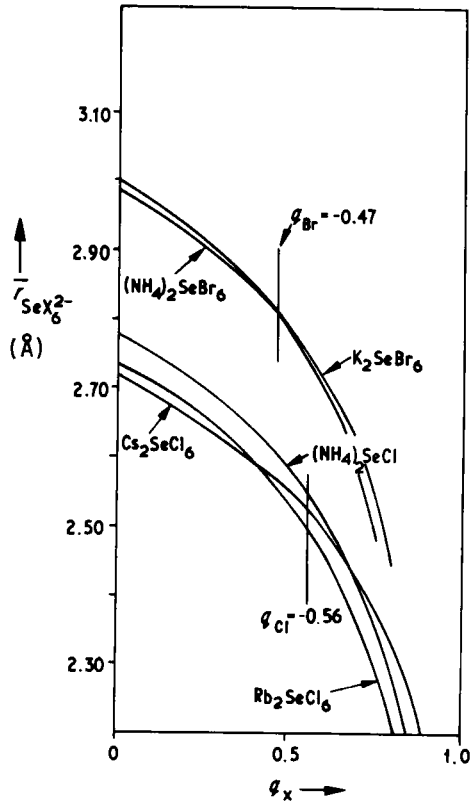


FIG. 29. Basic radius of the ions $SeCl_6^{2-}$ and $SeBr_6^{2-}$, corresponding to lattice potential energy minima, as a function of the charge, q_X, on the halogen atom of the ion.

iv. *"Basic" radius of ion* (Fig. 29)

$$\bar{r}_{SeCl_6^{2-}} = 2.52 \text{ Å}$$

No thermochemical data exist for these salts.

2. $SeBr_6^{2-}$: *Hexabromoselenate Ion*

a. Recent Studies

i. *Structures*

K_2SeBr_6 ($a_0 = 10.363$ Å, $u = 0.245$) (*74*)

$(NH_4)_2SeBr_6$ ($a_0 = 10.46$ Å, $u = 0.245$) (*74*)

ii. *Charge distribution*

$$q_{Br} = -0.47$$

iii. *Lattice energies*

$$U_{POT}(K_2SeBr_6) = 1379 \text{ kJ mol}^{-1}$$
$$U_{POT}[(NH_4)_2SeBr_6] = 1380 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 29)

$$\bar{r}_{SeBr_6^{2-}} = 2.81 \text{ Å}$$

No thermochemical data exists for these salts.

3. $TeCl_6^{2-}$: *Hexachlorotellurate Ion*

a. Recent Calculations

i. *Structures*

Rb_2TeCl_6 ($a_0 = 10.233$ Å, $u = 0.245$) (*74*) ($a_0 = 10.233$ Å, $u = 0.2468$) (*69*)

Cs_2TeCl_6 ($a_0 = 10.447$ Å, $u = 0.24$) (*74*)

Tl_2TeCl_6 ($a = 10.107$ Å, $u = 0.245$) (*74*)

$(NH_4)_2TeCl_6$ ($a_0 = 10.178$ Å, $u = 0.25$) (*74*) ($a_0 = 10.200$ Å, $u = 0.2478$) (*30*)

ii. *Charge distribution*

$$q_{Cl} = -0.68$$

iii. *Lattice energies*

$$U_{POT}(Rb_2TeCl_6) = 1321 \text{ kJ mol}^{-1} \text{ or } 1316 \text{ kJ mol}^{-1}$$
$$U_{POT}(Cs_2TeCl_6) = 1323 \text{ kJ mol}^{-1}$$
$$U_{POT}(Tl_2TeCl_6) = 1392 \text{ kJ mol}^{-1}$$
$$U_{POT}[(NH_4)_2TeCl_6] = 1318 \text{ kJ mol}^{-1} \text{ or } 1320 \text{ kJ mol}^{-1}$$

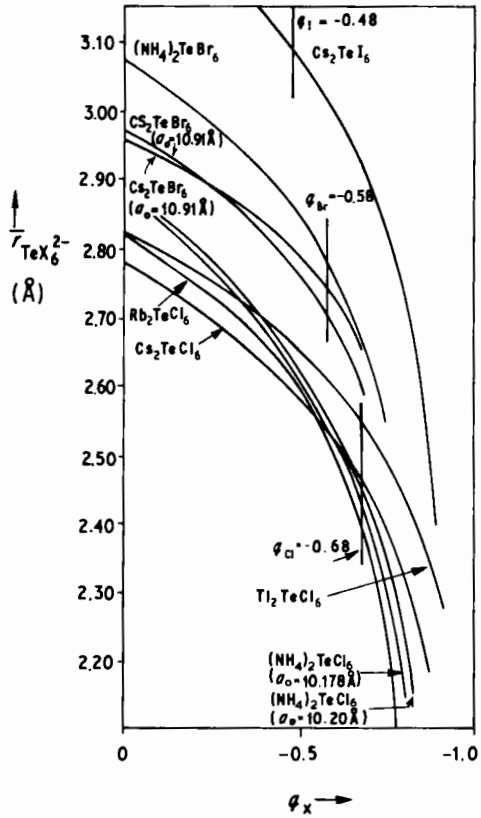


FIG. 30. Basic radii of the ions, $TeCl_6^{2-}$, $TeBr_6^{2-}$, and TeI_6^{2-}, corresponding to lattice potential energy minima, plotted as functions of the distributed charge in the ion.

iv. "*Basic*" *radius of ion* (Fig. 30)

$$\bar{r}_{TeCl_6^{2-}} = 2.41 \text{ Å}$$

v. *Enthalpy of formation of gaseous ion* (Fig. 31)

Ancillary data:

$\Delta H_f^0(K_2TeCl_6)(c) = -1167$ kJ mol^{-1} (*25*, *56*),

$\Delta H_f^0(Rb_2TeCl_6)(c) = -1231.8$ kJ mol^{-1} (*69*), -1251 kJ mol^{-1} (*25*, *26*).

Assigned value:

$$\Delta H_f^0(TeCl_6^{2-})(g) = -891 \pm 24 \text{ kJ mol}^{-1}$$

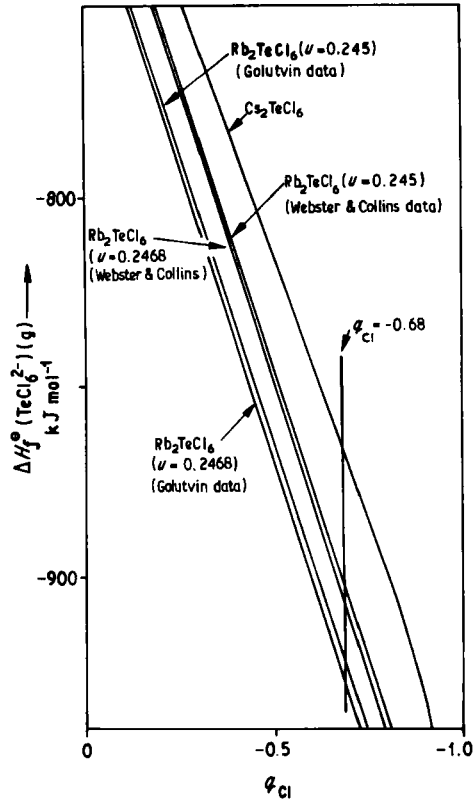


FIG. 31. Enthalpy of formation, $\Delta H_f^{\theta}(TeCl_6^{2-})(g)$, corresponding to a lattice potential energy minimum, as a function of charge q_{Cl} on the chlorine atom.

vi. *Halide ion affinities*

Ancillary data:

$$\Delta H_f^{\theta}(TeCl_4)(c) = -326 \text{ kJ mol}^{-1} \text{ (56)}$$

and

$$\Delta H_f^{\theta}(TeCl_4)(g) = -246 \text{ kJ mol}^{-1} \text{ (69)}.$$

Assigned values:

$$\overline{\Delta H}_{Cl(c)} = -73 \pm 24 \text{ kJ mol}^{-1}$$
$$\overline{\Delta H}_{Cl(g)} = -153 \pm 27 \text{ kJ mol}^{-1}$$

b. Derived Estimates

i. *Structure*

$$K_2TeCl_6\ (a_0 = 10.143\ \text{Å})\ (74)$$

ii. *Prediction of lattice energy*

$$U_{POT}(K_2TeCl_6) = 1318\ \text{kJ mol}^{-1}$$

c. Previous Calculations. Webster and Collins (*69*) and Jenkins and Smith (*40*) have considered the lattice energy of Rb_2TeCl_6. Their results are compared in Table I, and the thermodynamic estimates that they obtained are given below.

Webster and Collins (*69*):

$$\Delta H_f^{\theta}(TeCl_6^{2-})(g) = -804 \pm 71\ \text{kJ mol}^{-1}$$

$$\overline{\Delta H}_{Cl(g)} = -91 \pm 71\ \text{kJ mol}^{-1}$$

Jenkins and Smith (*40*).

$$\Delta H_f^{\theta}(TeCl_6^{2-})(g) = -1020\ \text{kJ mol}^{-1}$$

$$\overline{\Delta H}_{Cl(g)} = -304\ \text{kJ mol}^{-1}$$

Golutvin *et al.* (*25*, *26*):

$$\Delta H_f^{\theta}(TeCl_6^{2-})(g) = -1130 \pm 5\ \text{kJ mol}^{-1}$$

4. $TeBr_6^{2-}$: *Hexabromotellurate Ion*

a. Recent Studies

i. *Structures*

Cs_2TeBr_6 ($a_0 = 10.91$ Å, $u = 0.24$) (*74*) ($a_0 = 10.918$ Å, $u = 0.2468$) (*15*)

$(NH_4)_2TeBr_6$ ($a_0 = 10.728$ Å, $u = 0.2499$) (*65a*)

ii. *Charge distribution*

$$q_{Br} = -0.58$$

iii. *Lattice energies*

$$U_{POT}(Cs_2TeBr_6) = 1306 \text{ kJ mol}^{-1} \quad \text{or} \quad 1292 \text{ kJ mol}^{-1}$$
$$U_{POT}[(NH_4)_2TeBr_6] = 1294 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 30)

$$\bar{r}_{TeBr_6^{2-}} = 2.73 \text{ Å}$$

v. *Enthalpies of formation of gaseous ion*
Ancillary data:

$$\Delta H_f^{\theta}(K_2TeBr_6)(c) = -972 \text{ kJ mol}^{-1} \ (65a)$$

and

$$\Delta H_f^{\theta}(Cs_2TeBr_6)(c) = -1032 \text{ kJ mol}^{-1} \ (65a).$$

Assigned value:

$$\Delta H_f^{\theta}(TeBr_6^{2-})(g) = -661 \pm 40 \text{ kJ mol}^{-1}$$

vi. *Halide ion affinities*
Ancillary data:

$$\Delta H_f^{\theta}(TeBr_4)(c) = -190 \text{ kJ mol}^{-1} \ (56).$$

Assigned value:

$$\overline{\Delta H}_{Br(c)} = 21 \pm 40 \text{ kJ mol}^{-1}$$

5. TeI_6^{2-}: *Hexaiodotellurate Ion*

a. Recent Studies

i. *Structure*

$$Cs_2TeI_6 \ (a_0 = 11.721 \text{ Å}, u = 0.248) \ (74)$$

ii. *Charge distribution*

$$q_I = -0.48$$

iii. *Lattice energies*

$$\boxed{U_{POT}(Cs_2TeI_6) = 1246 \text{ kJ mol}^{-1}}$$

No thermochemical data exists for these salts.

6. $PoCl_6^{2-}$: *Hexachloropolonate Ion*

a. Recent Studies

i. *Structures*

$(NH_4)_2PoCl_6$ ($a_0 = 10.35$ Å, $u = 0.23$) (*74*)

ii. *Charge distribution*

$$q_{Cl} = -0.7$$

iii. *Lattice energies*

$$\boxed{U_{POT}(NH_4)_2PoCl_6 = 1338 \text{ kJ mol}^{-1}}$$

iv. "*Basic*" *radius of ion* (Fig. 32)

$$\boxed{\bar{r}_{PoCl_6^{2-}} = 2.60 \text{ Å}}$$

No thermochemical data exist for these salts.

7. $PoBr_6^{2-}$: *Hexabromopolonate Ion*

a. Recent Studies

i. *Structures*

Cs_2PoBr_6 ($a_0 = 11.01$ Å, $u = 0.24$) (*74*)

$(NH_4)_2PoBr_6$ ($a_0 = 10.84$ Å, $u = 0.24$) (*74*)

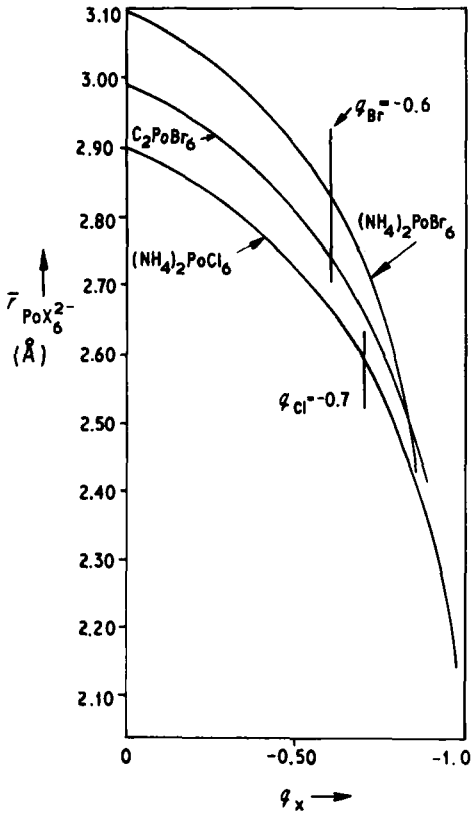


FIG. 32. Basic radii of $PoCl_6^{2-}$ and $PoBr_6^{2-}$, corresponding to lattice potential energy minima, as functions of the charge q_X on the halogen atom.

ii. *Charge distribution*

$$q_{Br} \simeq -0.60$$

iii. *Lattice energies*

$$U_{POT}(Cs_2PoBr_6) = 1286 \text{ kJ mol}^{-1}$$
$$U_{POT}((NH_4)_2PoBr_6) = 1292 \text{ kJ mol}^{-1}$$

iv. "*Basic*" *radius of ion* (Fig. 31)

$$\bar{r}_{PoBr_6^{2-}} = 2.78 \text{ Å}$$

No thermochemical data exist for these salts.

VI. Summary Tabulation of Rigorous Calculations

We give in Table III a summary of the lattice energies we have calculated rigorously; the table includes, in parentheses, occasional directly estimated values.

VII. Summary Tabulation of Derived Estimates

This section contains a number of "derived estimates" (Table IV) for the lattice energies of salts for which no full structural information is available. Equations (53)–(58) are used to derive the values from the literature a_0 values.

VIII. Discussion

A. Introduction

This article represents the first attempt to obtain lattice energies for transition metal salts A_2MX_6 on a comparative basis, and in doing this generates the possibility of commenting on donor–acceptor strengths and relative bond strengths of transition metal and main group ions of the type MX_6^{2-}.

In discussing the overall results we must establish the fact that many of the ancillary thermochemical and charge distribution data used must be regarded as *approximate* in that they both come from a multitude of sources and in that we have taken a given thermochemical value on its merit, if it was cited in the literature surveyed, although in the light of the results generated we have tried to be critical of such values. The charge distributions for the ions in question are *very tentative* in that they come from a variety of sources. The crystal structure data must also be of varying quality. In the light of these considerations we produce what we hope are qualitatively, if not *entirely* quantitatively, meaningful results, which should be strengthened by the further studies we intend. The maximum error likely in the absolute bond energy is probably of the order of $\pm$ 15 kJ mol^{-1}, which gives an indication of our notional precision.

The dispersion energies, U_{dd} and U_{qd}, in the present study are probably slightly high, resulting in a lattice energy that is also too high. This arises from the model used to calculate the dispersion terms (namely that of six X^- halide ions at the X atomic positions in the MX_6^{2-} ions).

The magnitudes used for U_{dd}, however, conform with all the studies in the literature, and so the comparison of the literature values with

the present work for $U_{POT}(A_2MX_6)$ undertaken below is unaffected by these considerations.

Calculations on TlCl, TlBr, and TlI exhibit a variation of $\bar{r}_{Tl^+}$ from salt to salt, which makes the subsequent assignment of $\bar{r}_{Tl^+}$ in relation to Tl_2MX_6 salts uncertain. Consequent errors for the salts Tl_2PtCl_6 and Tl_2SiF_6 will be larger than for salts with other cations.

B. Charge Distributions

For selected ions the literature contains a host of assessments of q_X, the charge on the halogen atom. For example in the ion $SnCl_6^{2-}$, q_{Cl} is quoted as -0.498 by Brill *et al.* (*8*), while Kubo and Nakamura (*50*) cite q_{Cl} equal to -0.66, Welsh *et al.* (*70*) quote -0.50, and the Jørgensen average (*42–45*) (Table I) gives -0.74. The question arises to which value we should assume in our studies and what difference such a choice makes to $U_{POT}(A_2MX_6)$. Our policy has been to take the values from the study of Brown *et al.* (*9*) in preference to those of Kubo and Nakamura (*50*), which are in turn taken in preference to the Jørgensen averages (*42–45*).

Taking K_2SnCl_6 as an example, using the structure of Brill *et al.* (*8*), we find that for a range of values of q_{Cl} from -0.498 to -0.74, $U_{POT}(K_2SnCl_6)$ varies from 1411 to 1329 kJ mol^{-1} (a variation of about 5%) and corresponds to 70 kJ mol^{-1} difference in lattice energy. It can be shown theoretically that if we take the Eq. (51):

$$\left(\frac{\partial U_{POT}}{\partial q_X}\right) = \left\{[\gamma_1 - \delta_1\phi_2] + 2(\gamma_2 - \delta_1\phi_3)q_X - \frac{(\phi_2 + 2\phi_3 q_X)(\delta_0 + 2\phi_0\delta_1)}{2(\phi_1 + \phi_2 q_X + \phi_3 q_X^2)^{1/2}}\right\} \tag{80}$$

and at $q_X = q_{Cl} = -0.50$, we have for K_2SnCl_6:

$$\left(\frac{\partial U_{POT}}{\partial q_X}\right)_{q_X=-0.5} = [\gamma_1 - \gamma_2 - \delta_1(\phi_2 - \phi_3)] - \frac{(\phi_2 - \phi_3)(\delta_0 + 2\phi_0\delta_1)}{2(\phi_1 - 0.5\phi_2 + 0.25\phi_3)^{1/2}} \tag{81}$$

$$= 296 \text{ kJ mol}^{-1} \text{ proton unit}^{-1} \tag{82}$$

which is the rate of variation found for $U_{POT}(K_2SnCl_6)$ in practice at $q_{Cl} = -0.50$. We see therefore that the choice of q_X is rather important, and hence consistent periodic trends of the type we have aimed to

select (Table I) in our choice of q_X are essential. The nonavailability of precise measures of q_X hampers the present work to some extent. The forthcoming attempts to examine salts A_2MX_6 possessing different crystal symmetry to the antifluorite arrangement promises a way around this difficulty.

C. Comparison of Lattice Energies Generated with Literature Values

We shall not concern ourselves in this study with the comparison of our present results with those originating from studies whose results are obtained by using the Born–Mayer (*6*), Born–Lande (*5*) or Kapustinskii (*46*) equations, since these approaches are known to generate effective lattice energies, which are on the whole too high. This leaves us with the comparison of results of Welsh *et al.* (*70*), Webster and Collins (*69*), Jenkins and Smith (*40*), and Jenkins (*36*) for $U_{POT}(A_2MX_6)$, which in turn requires comparison of values for the salts K_2SnCl_6, Rb_2SnCl_6, Cs_2GeCl_6, K_2PtCl_6, Rb_2TeCl_6, and K_2PbCl_6 (see Table V).

The agreement between the results for $U_{POT}(A_2MX_6)$ of Welsh *et al.* (*70*), who obtain their values using the following charge distributions: Cs_2GeCl_6 ($q_{Cl} = -0.467$), K_2SnCl_6 ($q_{Cl} = -0.50$), and Rb_2PbCl_6 ($q_{Cl} = -0.483$) is close to those of Jenkins and Pratt (who use the same structural data) in this study based on: Cs_2GeCl_6 ($q_{Cl} = -0.73$), K_2SnCl_6 ($q_{Cl} = -0.66$) and Rb_2PbCl_6 ($q_{Cl} = -0.63$). However comparison of

TABLE V

Comparison of Lattice Energies and Constituent Terms in Other Literature Calculations (kJ mol^{-1})

Salt	U_{ELEC}	q_X	U	U_R	$U_{POT}(A_2MX_6)$	Reference
Cs_2GeCl_6	1414	−0.467	166	172	1404	(*70*)
Cs_2GeCl_6	1305	−0.73	162	92	1375	This work
K_2SnCl_6	1394	−0.50	169	169	1370	(*70*)
K_2SnCl_6	1310	−0.66	113	60	1363	This work
Rb_2SnCl_6	1599	−0.3	131	143	1551	(*69*)
Rb_2SnCl_6	1302	−0.66	91	134	1259	(*40*)
Rb_2SnCl_6	1303	−0.66	129	71	1361	This work
Rb_2PbCl_6	1360	−0.483	141	161	1335	(*70*)
Rb_2PbCl_6	1283	−0.63	125	65	1343	This work
Rb_2TeCl_6	1578	−0.3	131	136	1533	(*69*)
Rb_2TeCl_6	1242	−0.68	92	136	1201	(*40*)
Rb_2TeCl_6	1239	−0.68	125	48	1316	This work

individual terms in Eq. (15), writing $U_{dd} + U_{qd} = U_D$, reveals notable differences (see Table V).

A recent discussion by Jenkins (*36*) centered on a less rigorous minimization method (but one whose results for K_2PtCl_6 (U_{POT} = 1468 kJ mol^{-1}) are almost identical to those obtained during the present approach) has drawn attention to the high repulsion energies generally assigned to salts of the general type A_2MX_6 by various workers. The values of U_R obtained by Brill *et al.* (*7*) are sometimes almost three times those obtained in this study whereas the dispersion terms differ by much less. Hence the lower U_{ELEC} value in our study (arising from the assignment of a higher $|q_X|$ value) is compensated for by the higher U_R term in the other study, giving overall agreement for $U_{POT}(A_2MX_6)$.

Turning now to the salts Rb_2SnCl_6 and Rb_2TeCl_6 and the works of Webster and Collins and Jenkins and Smith, which we compare to the present study in Table V, we find again that repulsion energies are much lower in the present study.

D. Enthalpies of Formation of Ions from Standard States, $\Delta H_f^{\theta}(MX_6^{2-})(g)$

A few specific comments on our calculated results should be dealt with first.

1. In the studies on the ions $TiCl_6^{2-}$, $TiBr_6^{2-}$, and $ZrCl_6^{2-}$ we have used Korol'kov and Effimov's (*48*) values for the enthalpies of formation of the salts from *gaseous atoms* and have "corrected" these to standard enthalpies of formation. The question of consistency of thermodynamic data used arises.

2. The $\Delta H_f^{\theta}(ZrCl_6^{2-})(g)$ value assigned in this study resulted from averaging the assigned values based on differing (*22, 48*) values for $\Delta H_f^{\theta}(Cs_2ZrCl_6)(c)$ in the literature. The former value being "corrected" as described in Comment 1 above.

3. In our calculations (Table III) we find that in general

$$U_{POT}(K_2MX_6) = U_{POT}[(NH_4)_2MX_6] \tag{83}$$

and in the absence of data for one salt we can estimate its lattice energy from that of the other. We have used this relation, Eq. (83), to estimate $U_{POT}(A_2MX_6)$ for $(NH_4)_2IrCl_6$ and K_2PdCl_6.

4. The value of $\Delta H_f^{\theta}((NH_4)_2SiF_6)(c)$ used in Section VG comes from Technical Note 270 (*56*), which is an updated version of Circular 500 (*61*), and is some 50 kJ mol^{-1} lower; however, $\Delta H_f^{\theta}(K_2SiF_6)(c)$,

$\Delta H_f^\theta(Rb_2SiF_6)(c)$, and $\Delta H_f^\theta(Cs_2SiF_6)(c)$ have been *deleted* rather than revised and, moreover, show unexpected variation going from the K^+ to the Cs^+ salt (the Cs_2SiF_6 enthalpy of formation appears to be too high).

If we deal only with the ammonium salt (the only enthalpy of formation value that has been revised), we obtain

$$\Delta H_f^\theta(SiF_6^{2-})(g) = -2275 \text{ kJ mol}^{-1}$$
$$\overline{\Delta H}_{F(g)} = -119 \text{ kJ mol}^{-1}$$
$$\Delta H_{hyd}^\theta(SiF_6^{2-})(g) = -985 \text{ kJ mol}^{-1}$$

and we regard these values as being more reliable than the assignments based on the K^+, Rb^+, and Cs^+ salts, despite the operation of the point charge approximation for the NH_4^+ ion.

Turning now to a comparison of our assigned values and other literature values, Table VI gives our assigned values of $\Delta H_f^\theta(MX_6^{2-})(g)$.

Brill *et al.* (*7*) obtained the values

$$\Delta H_f^\theta(GeCl_6^{2-})(g) = -956 \pm 84 \text{ kJ mol}^{-1}$$
$$\Delta H_f^\theta(SnCl_6^{2-})(g) = -1125 \pm 84 \text{ kJ mol}^{-1}$$
$$\Delta H_f^\theta(PbCl_6^{2-})(g) = -927 \pm 92 \text{ kJ mol}^{-1}$$

in the same numerical order as our values, but some 25, 29, and 13 kJ mol^{-1}, respectively, higher. We regard this as substantial agreement.

Webster and Collins (*69*) obtained

$$\Delta H_f^\theta(SnCl_6^{2-})(g) = -1070 \pm 70 \text{ kJ mol}^{-1}$$
$$\Delta H_f^\theta(TeCl_6^{2-})(g) = -804 \pm 70 \text{ kJ mol}^{-1}$$

and Jenkins and Smith (*40*) obtained

$$\Delta H_f^\theta(SnCl_6^{2-})(g) = -1256 \text{ kJ mol}^{-1}$$
$$\Delta H_f^\theta(TeCl_6^{2-})(g) = -1020 \text{ kJ mol}^{-1}$$

values, which bracket our present estimates, for reasons discussed in Section III on lattice energy. The latter calculation was based on the assumption that the Lewis acid strengths of $SnCl_4$ and $TeCl_4$ toward Cl^- are very nearly the same.

TABLE VI

SUMMARY OF DERIVED THERMODYNAMIC DATA (kJ mol^{-1} UNLESS OTHERWISE STATED) INCLUDING BOND ENERGIES $E(M-X)_{hom}$ AND $E(M-X)_{het}$ AND TOTAL COORDINATE BOND ENERGY (c.b.e.) = $6E(M-X)_{het}$ [Eq. (6)] FOR MX_6^{2-}.

Ion	$\overline{\Delta H}_{X(ss)}$ (ss)[a]	$\overline{\Delta H}_{X(ss)}$ Value	$\Delta H_f^{\theta}(MX_6^{2-})$ (g)	$\Delta H_{hyd}^{0}(MX_6^{2-})$ (g)	$\bar{r}_{MX_6^{2-}}$ (Å)	$\Delta H_f^{a}(MX_6^{2-})$ (g)	$\Delta H_f^{i}(MX_6^{2-})$ (−c.b.e) (g)	$\overline{E(M-X)}_{hom}$ bond energy	$\overline{E(M-X)}_{het}$ Coordinate bond energy	Total coordinate bond energy (c.b.e.) for MX_6^{2-} (eV).
$TiCl_6^{2-}$	(1)	−36	−1330	—	2.48	−2530	−9252	422	1542	95.9
	(g)	−76								
$TiBr_6^{2-}$	(c)	−58	−1142	—	2.61	−2281	−9148	380	1525	94.8
	(g)	−125								
$ZrCl_6^{2-}$	(c)	−54	−1526	—	2.47	−2863	−8252	477	1375	85.8
	(g)	−164								
$HfCl_6^{2-}$	(c)	(−158)	(−1640)	—	—	−2985	−8015	498	1336	83.1
	(g)	(−259)								
$NbCl_6^{2-}$	(c)	(−78)	(−1224)	—	—	−2678	−8765	446	1461	90.8
	(g)	(−171)								
$TaCl_6^{2-}$	(c)	(−102)	(−1275)	—	—	−2782	−8326	464	1388	86.3
	(g)	(−243)								
$MoCl_6^{2-}$	(c)	−102	−1070	—	2.54	−2454	−9721	409	1620	100.7
		(−73)	(−1041)			(−2424)	(−9691)	(404)	(1615)	(100.4)
	(g)	−192								
		(−163)								
WCl_6^{2-}	(c)	−46	−985	—	2.49	−2560	−8656	427	1443	89.7
	(g)	−152								
WBr_6^{2-}	(c)	−91	−705	—	2.72	−2223	−8464	371	1411	87.7

$ReCl_6^{2-}$	(c)	−66	−919	−709	2.54	−2416	−8900	403	1483	92.2
$ReBr_6^{2-}$	(c)	+82	−689	—	2.81	−2131	−8760	355	1460	90.8
$OsCl_6^{2-}$	(c) (g)	−5 −181	−752	—	2.54	−2269	−8976	378	1496	93.0
$IrCl_6^{2-}$	(g)	—	(−785)	(−706)	2.56	−2179	−8867	363	1478	91.9
NiF_6^{2-}	(g)	—	−1328	—	1.97	−2232	−11600	372	1933	120.2
$PdCl_6^{2-}$	(g)	—	(−734) (−765)	(−735)	2.61	(−1856)	(−10337)	(309)	(1723)	(107.1)
$PtCl_6^{2-}$	(c)	−37	−792	−757	2.59	−2085	−9461	348	1577	98.0
$PtBr_6^{2-}$	(c)	−18	−645	−703	2.85	−1879	−9400	313	1567	97.4
SiF_6^{2-}	(g)	−119 (−42)	−2275 (−2198)	−985 (−1071)	1.94	−3201 (−3124)	−11239 (−11162)	534 (521)	1873 (1860)	116.5 (115.6)
GeF_6^{2-}	(g)	−240	−1971	—	2.01	−2822	−10928	470	1821	113.2
$GeCl_6^{2-}$	(l) (g)	+43 +7	−981	—	2.43	−2085	−10033	348	1672	104.0
$SnCl_6^{2-}$	(l) (g)	−153 −192	−1156	−685	2.47	−2188	−9113	365	1519	94.5
$PbCl_6^{2-}$	(l) (g)	−119 −163	−940	—	2.48	−1863	−9107	311	1518	94.4
$TeCl_6^{2-}$	(c) (g)	−73 −153	−891	—	2.41	−1814	−9098	302	1516	94.3
$TeBr_6^{2-}$	(c)	−3	−661	—	2.73	−1529	−8958	255	1493	92.8

[a] (ss) = standard state.

DeJonge (*16, 17*) has calculated

$$\Delta H_f^a(PtCl_6^{2-})(g) = -2237 \text{ kJ mol}^{-1}$$
$$\Delta H_f^a(PtBr_6^{2-})(g) = -2000 \text{ kJ mol}^{-1}$$
$$\Delta H_f^a(PdCl_6^{2-})(g) = -1971 \text{ kJ mol}^{-1}$$

These values should be compared to our calculated values listed in Table VI, where the same order is preserved, but it should be noted that DeJonge's (*16,17*) values are derived from an extended Born–Lande (*5*) treatment.

E. Enthalpies of Hydration of Ions, $\Delta H^\theta_{hyd}(MX_6^{2-})(g)$

DeJonge (*16, 17*) obtains

$$\Delta H^\theta_{hyd}(PtCl_6^{2-})(g) = -602 \text{ kJ mol}^{-1}$$
$$\Delta H^\theta_{hyd}(PtBr_6^{2-})(g) = -584 \text{ kJ mol}^{-1}$$
$$\Delta H^\theta_{hyd}(PtI_6^{2-})(g) = -561 \text{ kJ mol}^{-1}$$
$$\Delta H^\theta_{hyd}(PdCl_6^{2-})(g) = -606 \text{ kJ mol}^{-1}$$

These values are similar to our values (Table VI) apart from the revised order of $\Delta H^\theta_{hyd}(PdCl_6^{2-})(g)$ and $\Delta H^\theta_{hyd}(PtCl_6^{2-})(g)$ due to the slightly larger "basic" radius we obtain for $PdCl_6^{2-}$ (2.61 Å) compared to $PtCl_6^{2-}$ (2.59 Å).

On the basis of our "basic" radii, we might expect the following trends of hydration enthalpies:

$$\Delta H^\theta_{hyd}(TiCl_6^{2-})(g) > \Delta H^\theta_{hyd}(ZrCl_6^{2-})(g)$$
$$\Delta H^\theta_{hyd}(MoCl_6^{2-})(g) > \Delta H^\theta_{hyd}(WCl_6^{2-})(g)$$
$$\Delta H^\theta_{hyd}(TcCl_6^{2-})(g) > \Delta H^\theta_{hyd}(ReCl_6^{2-})(g)$$
$$\Delta H^\theta_{hyd}(PdCl_6^{2-})(g) > \Delta H^\theta_{hyd}(PtCl_6^{2-})(g)$$
$$\Delta H^\theta_{hyd}(GeCl_6^{2-})(g) < \Delta H^\theta_{hyd}(SnCl_6^{2-})(g) < \Delta H^\theta_{hyd}(PbCl_6^{2-})(g)$$
$$\Delta H^\theta_{hyd}(SeCl_6^{2-})(g) > \Delta H^\theta_{hyd}(TeCl_6^{2-})(g)$$
$$\Delta H^\theta_{hyd}(PtCl_6^{2-})(g) < \Delta H^\theta_{hyd}(PtBr_6^{2-})(g)$$

Burgess and Cartwright (*10a*) have given single ion hydration enthalpies obtained from their thermochemical and lattice studies:

$$\Delta H^{\theta}_{hyd}(ReCl_6^{2-})(g) = -836 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{hyd}(ReBr_6^{2-})(g) = -784 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{hyd}(IrCl_6^{2-})(g) = -834 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{hyd}(PtCl_6^{2-})(g) = -844 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{hyd}(PtBr_6^{2-})(g) = -769 \text{ kJ mol}^{-1}$$

F. Halide Ion Affinities

Table VI gives the halide ion affinities for the process

$$MX_4(ss) + 2X^-(g) \xrightarrow{\overline{\Delta H}_{X(ss)}} MX_6^{2-}(g)$$

using Eq. (4) to calculate $\overline{\Delta H}_{X(ss)}$.

Westland *et al.* (*22, 51*) have given the relationships (68), (72), (75), (76), and (78). Taking their lattice energies from Lal and Westland (*51*) proposed lattice energy relationships, they would obtain

$$\overline{\Delta H}_{Cl(g)} = -26 \pm 5 \text{ kJ mol}^{-1} \text{ for } ZrCl_4$$

and

$$\overline{\Delta H}_{Cl(g)} = -37 \pm 14 \text{ kJ mol}^{-1} \text{ for } HfCl_4$$

and

$$\overline{\Delta H}_{Cl(g)} = +15 \text{ kJ mol}^{-1} \text{ for } NbCl_4$$

although they further quote

$$\overline{\Delta H}_{Cl(g)} = 3 \text{ kJ mol}^{-1} \text{ for } NbCl_4$$

and

$$\overline{\Delta H}_{Br(g)} = -4 \text{ to } +17 \text{ kJ mol}^{-1} \text{ for } NbBr_4$$

and

$$\overline{\Delta H}_{Cl(g)} = -23 \text{ kJ mol}^{-1} \text{ for } TaCl_4$$

and

$$\overline{\Delta H}_{Cl(g)} = +39 \text{ kJ mol}^{-1} \text{ for } SnCl_4.$$

Westland concludes that $ZrCl_4$ and $HfCl_4$ are somewhat better acceptors of Cl^- than $NbCl_4$ and that $ZrCl_4$ and $HfCl_4$ are markedly better acceptors of Cl^- than $SnCl_4$. $TaCl_4$ is found to be a better acceptor of Cl^- ion than $NbCl_4$.

Westland's (*22*, *51*) arguments are based on several assumptions given by relationships (81), (83), and (86); further, he assumes that

$$U_{POT}(K_2NbCl_6) = U_{POT}(K_2TaCl_6) = 1586 \text{ kJ mol}^{-1}$$

From our present calculations we find

$$U_{POT}(K_2SnCl_6) - U_{POT}(K_2ZrCl_6) = 24 \text{ kJ mol}^{-1} \quad (84)$$

$$U_{POT}(K_2NbCl_6) - U_{POT}(K_2ZrCl_6) = 36 \text{ kJ mol}^{-1} \quad (85)$$

$$U_{POT}(K_2HfCl_6) - U_{POT}(K_2ZrCl_6) = 16 \text{ kJ mol}^{-1} \quad (86)$$

$$U_{POT}(K_2TaCl_6) - U_{POT}(K_2NbCl_6) = 3 \text{ kJ mol}^{-1} \quad (87)$$

not too dissimilar to Westland's relationships. If we use our lattice energies in Eqs. (68), (72), (75), (76), and (80) we generate

$$\overline{\Delta H}_{Cl(g)} = -258 \text{ kJ mol}^{-1} \text{ for } ZrCl_4$$
$$\overline{\Delta H}_{Cl(g)} = -266 \text{ kJ mol}^{-1} \text{ for } HfCl_4$$
$$\overline{\Delta H}_{Cl(g)} = -196 \text{ kJ mol}^{-1} \text{ for } NbCl_4$$
$$\overline{\Delta H}_{Cl(g)} = -231 \text{ kJ mol}^{-1} \text{ for } TaCl_4$$
$$\overline{\Delta H}_{Cl(g)} = -184 \text{ kJ mol}^{-1} \text{ for } SnCl_4$$

The difference arises from the fact that our lattice energies are so much lower than those of Gelbman and Westland (*22*). The order of the acceptor power toward Cl^- ion is preserved:

$$HfCl_4 > ZrCl_4 > TaCl_4 > NbCl_4 > SnCl_4$$

Turning to our results in Table VI for the group designated IVA in Table II, we find the chloride ion affinities of the tetrahalides are in the order

$$HfCl_4 > ZrCl_4 > TiCl_4$$

For Group VA a similar group tendency is observed:

$$TaCl_4 > NbCl_4$$

in agreement with Westland's (*22*) order, although the absolute order for the five tetrahalides does not agree. For group VIA, however,

the order

$$WCl_4 < MoCl_4$$

is surprisingly found.

Makhida and Westland (*54a*) have calculated the order:

$$HfBr_4 > ZrBr_4 > SnBr_4$$

for acceptor power toward Br^-. We cannot compare results from this study since no full crystal structure determinations for A_2HfBr_6, A_2ZrBr_6 and A_2SnBr_6 salts are available.

For the main group IVB we find

$$GeCl_4 < SnCl_4 > PbCl_4$$

$$SnCl_4 > TeCl_4$$

Few intercomparisons can be made for the tetrabromides owing to the sparseness of the data.

G. Bond Strengths

The following processes give, to varying extents, a measure of the M—X bond strength:

$$M(g) + 6X(g) + 2\bar{e} \rightarrow MX_6^{2-}(g)\ \Delta H_f^a(MX_6^{2-})(g)$$

$$M^{4+}(g) + 6X^-(g) \rightarrow MX_6^{2-}(g)\ \Delta H_f^i(MX_6^{2-})(g)$$

the former involving the enthalpy of formation of the gaseous MX_6^{2-} ion from atoms; the latter, from ions.

The above thermodynamic quantities are interrelated thus:

$$\Delta H_f^\theta(MX_6^{2-})(g) - 3D_{X_2} - \Delta H_{sub}^\theta(M)(c) = \Delta H_f^a(MX_6^{2-})(g) \quad (88)$$

$$\Delta H_f^a(MX_6^{2-})(g) - \sum_{n=1}^{4} I_n - 6A_X = \Delta H_f^i(MX_6^{2-})(g) \quad (89)$$

where D_{X_2} is the dissociation energy of $X_2 : X_2(ss) \rightarrow 2X(g)$; $\Delta H_{sub}^\theta(M)(c)$ is the enthalpy of the process: $M(c) \rightarrow M(g)$; $\sum_{n=1}^{4} I_n$ represents the ionization potential of the process: $M(g) \rightarrow M^{4+}(g)$; A_X is the electron affinity of $X : X(g) \rightarrow X^-(g)$; I_n is the ionization potential corresponding to the process: $M^{(n-1)+}(g) \rightarrow M^{n+}(g)$.

The bond energies $\overline{E(M-X)}_{het}$ and $\overline{E(M-X)}_{hom}$ are related to the thermodynamic quantities in equations (6) and (5), respectively. We confine our comparisons of bond strengths to a discussion of the heterolytic bond energy, $\overline{E(M-X)}_{het}$, although Table VI cites the values of both.

Comparison of the bond strengths, $\overline{E(M-X)}_{het}$ obtained (Table VI) as described in Section I,B of this chapter, leads to:

(i) Ni—F > Si—F > Ge—F

(ii)
$$\begin{array}{ccccccccccccc} & & \text{Ti—Cl} & & & & & & & & & & \\ & & \vee & & & & & & & & & & \\ \text{Zr—Cl} & < & \text{Nb—Cl} & < & \text{Mo—Cl} & & & < & & & & & \text{Pd—Cl} \\ \vee & & \vee & & \vee & & & & & & & & \vee \\ \text{Hf—Cl} & < & \text{Ta—Cl} & < & \text{W—Cl} & < & \text{Re—Cl} & < & \text{Os—Cl} & > & \text{Ir—Cl} & < & \text{Pt—Cl} \end{array}$$

(iii)
$$\begin{array}{l} \text{Ge—Cl} \\ \vee \\ \text{Sn—Cl} \sim \text{Te—Cl} \\ \wr \\ \text{Pb—Cl} \end{array}$$

(iv) Ti—Br > W—Br < Re—Br < Pt—Br

In all cases:

$$M—F > M—Cl > M—Br$$

These trends are in line with chemical prediction (*38a*), but are almost without exception *reversed* by consideration of $\overline{E(M-X)}_{hom}$ values.

IX. Concluding Remarks

The aim of this review has been to collect the few lattice energy calculations already in existence and blend these into the framework of our newly proposed minimization method, which has generated the vast amount of data included in this chapter. Far from concluding this study, this is rather the commencement. The reader will note that the review concentrates on the attainment of lattice energies and leaves open the discussion of the thermodynamic data obtained with a view to further examination in the light of the studies on similar A_2MX_6 salts having different crystal structures.

We repeat our plea made in the introduction for continued interest in the obtaining of crystal structure data and ancillary thermodynamic

data for such salts, and would be pleased to be informed about further studies or about studies omitted from this chapter.

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X. Appendix

Since this chapter was written, a number of additional studies have been undertaken by the author. In order of likely appearance in print these are:

(i) A study and fuller discussion of the bond strengths and double halide ion affinities derived from the present study (Section VIII,F and G) with some estimates for metal–bromide bond strengths (*A1*).

(ii) Following some measurements by Makhija and Westland (*A2*) of:

$$\Delta H_f^{\theta}(K_2SeCl_6)(c) = -1076 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(Rb_2SeCl_6)(c) = -1103 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(K_2SeBr_6)(c) = -876 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(Rb_2SeBr_6)(c) = -907 \pm 2 \text{ kJ mol}^{-1}$$

the lattice energies of Rb_2SeCl_6 (Section V,I,1,a,iii) and K_2SeBr_6 (Section V,I,2,a,iii) are used to generate:

$$\Delta H_f^{\theta}(SeCl_6^{2-})(g) = -684 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(SeBr_6^{2-})(g) = -525 \text{ kJ mol}^{-1}$$

which in turn lead to halide ion affinity values, corresponding to the process:

$$2X^-(g) + SeX_4(c) \xrightarrow{\overline{\Delta H}_{X(c)}} SeX_6^{2-}(g)$$

of

$$\overline{\Delta H}_{Cl(c)} = -13 \text{ kJ mol}^{-1}$$

$$\overline{\Delta H}_{Br(c)} = +18 \text{ kJ mol}^{-1}$$

which can be compared to the Te values in Table VI. See Jenkins *et al.* (*A3*).

(iii) A further theoretical development (*A4*) made has enabled us to make a complete study of the salts A_2MX_6 having noncubic lattices (*A5*). Careful discussion and consideration of the literature crystal structure data for these salts is made and calculations are carried out for: M=Ti, Zr, Hf, Mo, Mn, Re, Rh, Pt, Si, Ge, X=F; M=Ce, Th, U, Pu, Bk, X=Cl; and M=Te, X=Br. These calculations enable us to predict enthalpies of formation for the ions:

$$\Delta H_f^{\theta}(TiF_6^{2-})(g) = -2321 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(SiF_6^{2-})(g) = -2295 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(GeF_6^{2-})(g) = -1973 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(TeBr_6^{2-})(g) = -682 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(ThCl_6^{2-})(g) = -1718 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(UCl_6^{2-})(g) = -1546 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\theta}(PuCl_6^{2-})(g) = -1527 \text{ kJ mol}^{-1}$$

halide ion affinites for:

TiF_4:

$$\overline{\Delta H}_{F(c)} = -130 \text{ kJ mol}^{-1}$$

$$\overline{\Delta H}_{F(g)} = -228 \text{ kJ mol}^{-1}$$

SiF_4:

$$\overline{\Delta H}_{F(g)} = -138 \text{ kJ mol}^{-1}$$

GeF_4:

$$\overline{\Delta H}_{F(g)} = -242 \text{ kJ mol}^{-1}$$

$TeBr_4$:

$$\overline{\Delta H}_{Br(c)} = -24 \text{ kJ mol}^{-1}$$

$ThCl_4$:

$$\overline{\Delta H}_{Cl(c)} = -34 \text{ kJ mol}^{-1}$$

UCl_4:

$$\overline{\Delta H}_{Cl(c)} = -3 \text{ kJ mol}^{-1}$$

$PuCl_4$:

$$\overline{\Delta H}_{Cl(c)} = -115 \text{ kJ mol}^{-1}$$

and enthalpy of hydration of SiF_6^{2-}:

$$\Delta H^{\theta}_{hyd}(SiF_6^{2-})(g) = -965 \text{ kJ mol}^{-1}$$

and heterolytic and homolytic bond strengths. Agreement, where comparison with cubic salt calculations is possible (SiF_6^{2-}, GeF_6^{2-} and $TeBr_6^{2-}$), is impressive in view of the fact that noncubic calculations do not require estimates of the charge distribution in the ion.

(iv) In a study of the hydrolysis of alkali metal hexachloro and hexabromo tungstates (IV) and rhenates (IV), Burgess *et al.* (*46*) have obtained a value, $\Delta H_f^{\theta}(WBr_4)(c) = -300$ kJ mol^{-1}, at variance with currently accepted literature value cited in this chapter (*11*, *56*). This value and others determined in this recent study lead us to two halide ion affinities for WCl_4:

$$\Delta H_{Cl(c)} = -70 \text{ kJ mol}^{-1}$$

$$\Delta H_{Cl(g)} = -176 \text{ kJ mol}^{-1}$$

(previous values in Section V,D,3,vi contain the above values within their stated ranges).

For WBr_4:

$$\overline{\Delta H}_{Br(c)} = -50 \text{ kJ mol}^{-1}$$

(this value supersedes the value of Section V,D,4,vi).

For $ReCl_4$:

$$\overline{\Delta H}_{Cl(c)} = -90 \text{ kJ mol}^{-1}$$

(previous value in Section V,E,4,vii contains the above within stated range).

For $ReBr_4$:

$$\overline{\Delta H}_{Br(c)} = -80 \text{ kJ mol}^{-1}$$

(very close to value quoted in this chapter, Section V,E,5,vi).

The hydration studies lead us to a value:

$$\Delta H^{\theta}_{hyd}(ReCl_6^{2-})(g) = -740 \text{ kJ mol}^{-1}$$

not previously assigned.

(v) The fifth and most recent study (*A7*) contains some measurements of the enthalpies of solution of some hexafluorosilicates ($Na^+ = +30.8 \pm 1.1$ kJ mol^{-1}; $K^+ = +73.0 \pm 2.0$ kJ mol^{-1}; $Rb^+ = +86.1 \pm 3.3$ kJ mol^{-1}; $Cs^+ = +131.7 \pm 0.9$ kJ mol^{-1}; $NH_4^+ = +33.8 \pm 0.9$ kJ mol^{-1} and $Ba^{2+} = +40.5 \pm 0.3$ kJ mol^{-1}); hexafluorotitanates ($K^+ = +74.0 \pm 1.8$ kJ mol^{-1} and $Cs^+ = +125.8 \pm 2.8$ kJ mol^{-1}); hexafluoromanganates ($K^+ = +61.1 \pm 1.1$ kJ mol^{-1}); hexafluororhenates ($Na^+ = +32.9 \pm 1.5$ kJ mol^{-1}, $K^+ = +63.0 \pm 0.3$ kJ mol^{-1}; $Cs^+ = +112.9 \pm 0.2$ kJ mol^{-1} and $Ba^{2+} = +35.4 \pm 1.2$ kJ mol^{-1}) and hexafluoruthenates ($K^+ = +59.4 \pm 1.5$ kJ mol^{-1}). From these studies and the associated lattice energies we assign:

$\Delta H^{\theta}_{hyd}(SiF_6^{2-})(g) = -971$ kJ mol^{-1}
$\Delta H^{\theta}_{hyd}(TiF_6^{2-})(g) = -881$ kJ mol^{-1}
$\Delta H_f^{\theta}(MnF_6^{2-})(g) = -1823$ kJ mol^{-1}
$\Delta H^{\theta}_{hyd}(MnF_6^{2-})(g) = -912$ kJ mol^{-1}
$\Delta H^{\theta}_{hyd}(ReF_6^{2-})(g) = -903$ kJ mol^{-1}
$\Delta H_f^{\theta}(ReF_6^{2-})(g) = -1961$ kJ mol^{-1}

Such studies are continuing.

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