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Group 3 Tetrahalide Salts, Lattice Energies and Thermodynamic Parameters. The $AlCl_4^-$ and $GaCl_4^-$ Ions

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Received June 13, 1975 AIC50425O

Gearhart, Beck, and Wood,[1] in this journal, have evaluated the enthalpies of formation of the gaseous tetrachloroaluminate ion, $\Delta H_f^0(AlCl_4^-)(g)$, and the tetrachlorogallate ion, $\Delta H_f^0(GaCl_4^-)(g)$. Assuming a value of q_{Cl}, the charge on the chlorine atoms of the ions $AlCl_4^-$ and $GaCl_4^-$, of −0.39 (equal to the average of the range of values selected for their calculations) the above workers obtain values $\Delta H_f^0(AlCl_4^-)(g) = -1188 \pm 28$ kJ mol^{-1} (-284 ± 7 kcal mol^{-1}) and $\Delta H_f^0(GaCl_4^-)(g) = -1029 \pm 28$ kJ mol^{-1} (-246 ± 7 kcal mol^{-1}) from a consideration of the lattice energies of representative salts. The contention of the present note is that the assumption regarding the constancy of q_{Cl} in the two ions, $AlCl_4^-$ and $GaCl_4^-$, which seems at variance with published electronegativity values (Ga 1.82, Al 1.47),[2] (Ga 1.81, Al 1.61),[3] and (Ga 1.95, Al 1.81),[4] is unnecessary. Moreover, if q_{Cl} is retained as a variable parameter throughout the treatment it can be determined for each of the ions individually and coincident with the determination of the enthalpies of formation of the ions. The assigned thermodynamic parameters are then determined with more certainty.

The equivalence of the equation of Gearhart[5] for the evaluation of the repulsion component of the lattice energy of a crystal lattice and the equation of Jenkins and Waddington[6] is demonstrated.

Theoretical Section

For group 3 halides of general formula $N(MCl_4)$ the following thermochemical cycle can be employed:

$$\begin{tikzcd}
N(MCl_4)(c) \arrow[rr, "{\Delta E[N(MCl_4)] + 2RT}"] & & N^+(g) + MCl_4^-(g) \\
& N(c) + M(c) + 2Cl_2(g) \arrow[ul, "{\Delta H_f^0[N(MCl_4)](c)}"] \arrow[ur, "{\Delta H_f^0(N^+)(g) + \Delta H_f^0(MCl_4^-)(g)}"'] &
\end{tikzcd}$$

where $\Delta E[N(MCl_4)]$ is the total internal energy change in the lattice energy step of the above cycle and is related to the total lattice potential energy, U_{pot}, defined as:

$$U_{pot}[N(MCl_4)] = U_{elec} + U_D - U_R \tag{1}$$

where U_{elec}, U_D, and U_R are the electrostatic, dispersion, and repulsion energies of the crystalline lattice, respectively, by the equation:[7]

$$\Delta E[N(MCl_4)] = U_{pot}[N(MCl_4)] - 3RT \tag{2}$$

From the cycle therefore:

$$U_{pot}[N(MCl_4)] - RT = \Delta H_f^0(N^+)(g) + \Delta H_f^0(MCl_4^-)(g) - \Delta H_f^0[N(MCl_4)](c) \tag{3}$$

If, as described in detail elsewhere,[8-10] we write the electrostatic lattice energy of the complex salt as a function of the distributed charge on the terminal chlorine atoms of the complex ion:

$$U_{elec} = \sum_{i=0}^{2} A_i q_{Cl}^i \tag{4}$$

then we write the enthalpy of formation of the complex ion also as a function of q_{Cl}:

$$\Delta H_f^0(MCl_4^-)(g) = \sum_{i=0}^{2} B_i q_{Cl}^i \tag{5}$$

A plot of $\Delta H_f^0(MCl_4^-)(g)$ vs. q_{Cl} for compounds where the gegenion N^+ varies, can be used to estimate not only the enthalpy of formation of the complex ion, which is independent of the nature of N^+, but also of the charge distribution on the ion as defined by q_{Cl}.

Results

Gearhart, Beck, and Wood[1] have considered, inter alia, the salts $Na(AlCl_4)$, $Cs(AlCl_4)$, $Cs(GaCl_4)$, and $Ga(GaCl_4)$, for which they have calculated the electrostatic energy, U_{elec}, for the three specified charge distributions (corresponding to q_{Cl} values of 0.0, −0.2, and −1.0). U_R, the repulsion energy, was calculated from the equation[5]

$$U(\delta^{OK})_{rep} = -\left(\frac{\rho}{a_0}\right)\left[U_{coul} + 6U_{vdw} + e^2\left(\frac{\partial M_\delta}{\partial \delta}\right)\right] \tag{6}$$

where, using the notation of eq 1:

$$U(\delta^{OK})_{rep} = U_R \tag{7}$$

$$U_{coul} = -U_{elec} \tag{8}$$

$$U_{vdw} = -U_D \tag{9}$$

and a_0 is the lattice constant, ρ is the repulsion constant (0.345 Å), and M_δ is the electrostatic Madelung constant referred to δ, the cube root of the molecular volume. From the above equation it can be inferred that if U_{elec} can be written in the form of eq 4 then U_R is also a quadratic function of q_{Cl}, within the applicability of eq 6

$$U_R = \sum_{i=0}^{2} C_i q_{Cl}^i \tag{10}$$

and hence in eq 5;

$$B_0 = A_0 - C_0 + U_D - RT - \Delta H_f^0(N^+)(g) - \Delta H_f^0[N(MCl_4)](c) \tag{11}$$

$$B_1 = A_1 - C_1 \tag{12}$$

$$B_2 = A_2 - C_2 \tag{13}$$

The above workers have also calculated the dispersion energy of the lattices.

As described below we can carry the parameter q_{Cl} through the calculation and determine it along with the thermodynamic parameters of the problem.

From the U_{elec} and U_R values quoted by Wood et al. we can obtain the constants in eq 4 and 10. These two equations are then combined, via the relationships 11, 12, and 13, into equations of the form of (5) for each complex ion. Solution

Table I. Parameterization of Equation for the Determination of Enthalpies of Formation and Charge Distributions of $AlCl_4^-$ and $GaCl_4^-$ [a]

	$AlCl_4^-$		$GaCl_4^-$	
	$Na(AlCl_4)$	$Cs(AlCl_4)$	$Cs(GaCl_4)$	$Ga(GaCl_4)$
U_{elec} A_0	555.34	502.62	499.74	522.41
A_1	−2.30	76.57	80.58	−165.43
A_2	58.78	63.81	67.15	−137.86
U_R C_0	73.38	73.09	72.88	82.30
C_1	−19.28	−3.39	−7.07	−0.38
C_2	−13.76	10.21	5.44	15.94
U_D	58.57	85.35	84.52	77.40
$\Delta H_f{}^0(N^+)(g)$	609.8[11]	458.6[12]	458.6[12]	861.9[11]
$\Delta H_f{}^0N(MCl_4)(c)$	−1140.1[1]	−1221.7[1]	−1054.0[1]	−703.7[1]
$\Delta H_f{}^0(MCl_4^-)(g)$ B_0	−1211.94	−1167.93	−1004.08	−1050.60
B_1	16.99	79.95	87.65	−165.06
B_2	72.55	53.60	61.71	−153.80
U_{pot}	555.8	486.4	494.5	547.3

[a] Energies in kJ mol^{-1}.

of the resulting equations enables an assignment to be made for the enthalpies of formation and for the charges.

The results are tabulated in Table I and the solution of the equations of the form (5) is illustrated graphically in Figure 1 and gives the results, for $AlCl_4^-$:

$$q_{Cl} = -0.59 \tag{14}$$

$$\Delta H_f{}^0(AlCl_4^-)(g) = -1196 \text{ kJ mol}^{-1} \tag{15}$$

and for $GaCl_4^-$:

$$q_{Cl} = -0.23 \text{ or } -0.94 \tag{16}$$

$$\Delta H_f{}^0(GaCl_4^-)(g) = -1021 \text{ or } -1032 \text{ kJ mol}^{-1} \tag{17}$$

An interesting feature, shown in Figure 1, is that the curves for the case of $GaCl_4^-$ have two intersections R and Q.

Discussion

There are several points of interest. (i) Q corresponds to the $GaCl_4^-$ ion having q_{Ga} = +2.76 and q_{Cl} = −0.94; R corresponds to q_{Ga} = −0.08 and q_{Cl} = −0.23. The point Q represents an uncommonly large difference in charge; in view of the known electronegativities, Q is far less plausible than R as a discriminant for the determination of q_{Cl} and $\Delta H_f{}^0$. We therefore assign:

$$\Delta H_f{}^0(GaCl_4^-)(g) = -1021 \text{ kJ mol}^{-1}$$

$$q_{Cl} = -0.23$$

(ii) From the electronegativity values cited earlier we should expect, since gallium is more electronegative than aluminum, that q_{Cl} in the gallium complex ion should be less negative than the corresponding value in the $AlCl_4^-$ ion. This is the case if we accept the argument above. Hence:

$$\Delta H_f{}^0(AlCl_4^-)(g) = -1196 \text{ kJ mol}^{-1}$$

$$q_{Cl} = -0.59$$

(iii) The method of treatment used in this paper enables $\Delta H_f{}^0$ values to be obtained with more certainty. The accuracy is now increased from that represented by the spread of arbitrarily chosen data[1] to the accuracy with which each individual calculation can be made.

(iv) The total lattice potential energies of the salts considered can now be estimated on the basis of our conclusions about q_{Cl}.

$$U_{pot}[Na(AlCl_4)] = 555.8 \text{ kJ mol}^{-1}$$

$$U_{pot}[Cs(AlCl_4)] = 486.4 \text{ kJ mol}^{-1}$$

$$U_{pot}[Cs(GaCl_4)] = 494.5 \text{ kJ mol}^{-1}$$

$$U_{pot}[Ga(GaCl_4)] = 547.3 \text{ kJ mol}^{-1}$$

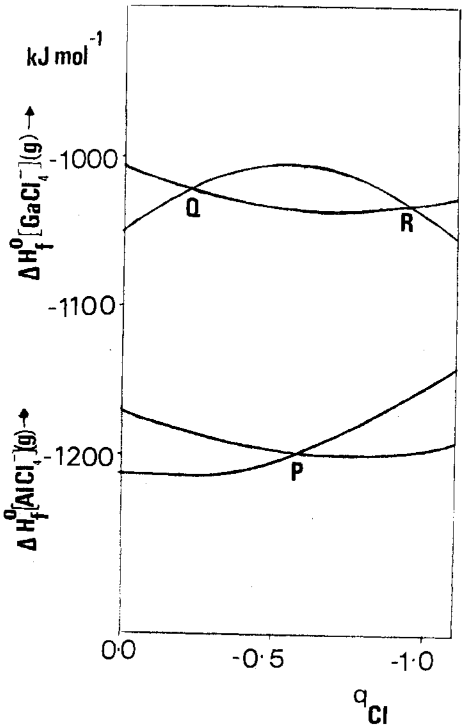

Figure 1. Enthalpies of formation of $GaCl_4^-$ and $AlCl_4^-$ ions.

(v) Gearhart, Beck, and Wood continue their paper with evaluations of the enthalpies of formation of $GaBr_4^-$ and $AlBr_4^-$ ions. In view of the agreement of the present results from the chloride moieties with their values it would seem that their bromide results should be reliable although their error estimates are probably too large.

(vi) Equation 1 can be written in the form:

$$U_{pot}[N(MCl_4)] = U_{elec} + U_D - U_R \tag{18}$$

$$= \frac{K}{a_0}M_{elec} + \frac{C}{a_0{}^6} - B\exp(-a_0/\rho) \tag{19}$$

where K is the conversion factor from e^2 Å^{-1} to kJ mol^{-1} and where a_0 is the cell constant. Differentiating with respect to a, we have:

$$\left(\frac{\partial U_{pot}[N(MCl_4)]}{\partial a}\right)_{a=a_0} = -\frac{K}{a_0{}^2}M_{elec} + \frac{K}{a_0}\left(\frac{\partial M_{elec}}{\partial a}\right) - \frac{6C}{a_0{}^7} + \frac{B}{\rho}\exp\left(-\frac{a}{\rho}\right) \tag{20}$$

$$\left(\frac{\partial U_{pot}[N(MCl_4)]}{\partial a}\right)_{a=a_0} = 0 \tag{21}$$

hence

$$B = \frac{\rho}{a_0}\left[\frac{K}{a_0}M_{elec} - K\left(\frac{\partial M_{elec}}{\partial a}\right) + 6U_D\right]\exp\left(\frac{a}{\rho}\right) \tag{22}$$

and since

$$U_R = B\exp(-a/\rho) \tag{23}$$

then

$$U_R = \frac{\rho}{a_0}\left[U_{elec} - K\left(\frac{\partial M_{elec}}{\partial a}\right) + 6U_D\right] \tag{24}$$

This equation compares well to Gearhart's eq 6 if we take into account their different sign convention as expressed in eq 7, 8, and 9 and equate $K = e^2$. The only difference is that eq 24 replaces $(\partial M_\delta/\partial\delta)$ by $(\partial M_{\mathrm{elec}}/\partial a)$. However, we can show that:

$$(\partial M_{\mathrm{elec}}/\partial a) = (\partial M_\delta/\partial\delta) \qquad (25)$$

and hence the equations are identical.

Registry No. Na(AlCl$_4$), 7784-16-9; Cs(AlCl$_4$), 17992-03-9; Cs(GaCl$_4$), 21646-31-1; Ga(GaCl$_4$), 24597-12-4; AlCl$_4^-$, 17611-22-2; GaCl$_4^-$, 15201-06-6.

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The Ligand-Field Spectrum of Niobium(IV) in Fluoride Melts[1]

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Received July 10, 1975 AIC50477D

Ligand-field spectra of the second-row transition-metal ions have not received as much attention as those of the first row, and consequently, rather little is known about the coordination behavior of these ions when they occur in dilute solutions. A continuing study at this laboratory is concerned with the characterization of niobium redox chemistry in fluoride melts by absorption spectroscopy. A prerequisite to this study is that the species involved in the redox equilibria and their absorption spectra be identified. High coordination numbers about the metal ions are favored in fluoride systems due to the size of the ligand and, as a result, some interesting spectra have been observed. An earlier paper[2] described the coordination behavior of Nb(IV) in the compound K$_3$NbF$_7$ and in this report its spectrum and behavior in fluoride melts are described.

Experimental Section

The spectrum of Nb(IV) in fluoride melts was obtained by dissolving either NbF$_4$ or K$_3$NbF$_7$ in a LiF–BeF$_2$ solvent. The preparation and characterization of these salts have been described before in detail.[2] Briefly, the experimental procedure[3] was as follows. A background spectrum of the molten LiF–BeF$_2$ (66–34 mol % or 48–52 mol %) was measured in a diamond-windowed graphite spectrophotometric cell at 550°C. The solvent and cell assembly were then cooled to room temperature and transported to a helium glove box of less than 1 ppm H$_2$O and O$_2$ content. There a weighed amount of solute was added to the top of the frozen salt. The cell was returned to the spectrophotometric furnace and reheated to 550°C. After the solvent melted, the solution was stirred with a platinum rod to ensure complete dissolution of the solute.

Absorption spectra were measured on a Cary 14H recording spectrometer equipped with a digital output accessory. The solvent background spectrum was subtracted from the solution spectrum using standard computing techniques.

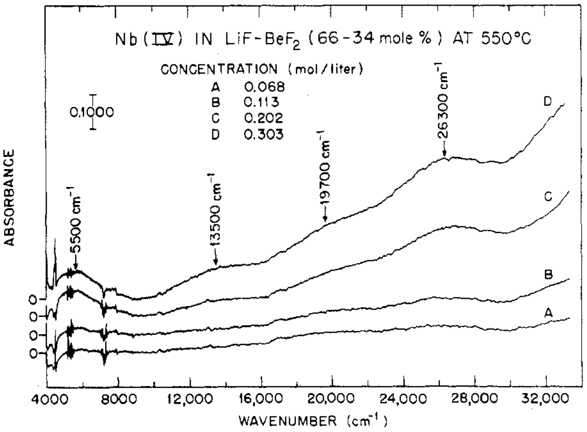

Figure 1. Nb(IV) in LiF–BeF$_2$ (66–34 mol %) at 550°C.

Results

Spectra of Nb(IV), which were recorded using the K$_3$NbF$_7$ in LiF–BeF$_2$ (66–34 mol %) solution, are shown in Figure 1. Other spectra, not shown here, were measured using NbF$_4$ solutions and were found to be identical with those in Figure 1. Because the binary salt was easier to handle and dissolved more readily in the melt, most of the work reported here was performed using it as a solute. No change in the Nb(IV) spectrum was observed in going to the LiF–BeF$_2$ (48–52 mol %) melt.

The spectra fade after sitting for several days at 550°C presumably because of a reaction of the niobium species with the graphite spectrophotometric cell. At higher temperatures (600–700°C) the loss of Nb(IV) occurs within a few hours. No new bands appear as a result, suggesting that the products of the reaction are *not soluble* niobium species with valences less than five.[4]

The four bands were found to obey the Beer–Lambert law within the accuracy of the baseline determination for concentration changes up to 0.303 mol/l. However, the test should be qualified in the 5500-cm^{-1} region because of rapidly changing instrument parameters which occur at the ir limit and are evident in Figure 1 by the abrupt drop-off of the curves at 4000 cm^{-1}. As a result, the position of the band at 5500 cm^{-1} is not considered to be very accurate.

The Beer–Lambert behavior in the 4000–30000 cm^{-1} region indicates that either a single species is present in solution or, if there is more than one, their concentrations are in constant proportion at all the concentrations studied. As the temperature was increased up to 700°C, the spectra broadened slightly, but did not shift perceptibly in area. The spectra faded at these temperatures (as mentioned earlier) and did not return when the temperature was dropped. If there had been more than one species in solution, the change in temperature would be expected to produce a much larger change in the spectrum, and therefore, it is concluded that the spectrum in Figure 1 arises from a single Nb(IV) species.

The species giving rise to the spectrum in Figure 1 can be identified by the relationship of its spectrum to that of crystalline K$_3$NbF$_7$.[2] The spectrum of K$_3$NbF$_7$ consists of four bands which are assigned on the basis of a slightly distorted D_{5h} complex as indicated in Table I. Thermal disordering of the ligands with increasing temperature causes further distortions from D_{5h} symmetry and results in increased splittings for the degenerate e states of the Nb(IV) ion. In the limit defined by the melting point of the crystal, all bands should be completely separated. These would be assigned as arising from a seven-coordinated species with C_1 symmetry.