NOTES

Thermodynamic Properties of Alkali Metal Fluoborates and the Fluoborate Ion

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A considerable number of structural, spectroscopic and thermal studies have been made on alkali metal and NH_4^+ fluoborates in the solid state and in solution. The data available from these investigations can be used to calculate a number of the thermodynamic properties of the alkali metal and ammonium fluoborates and of the fluoborate ion.

The infrared and Raman spectra of $NaBF_4$, KBF_4 and NH_4BF_4 have been studied[2-4] in the solid state (films and mulls) and in solution. The vibrational frequencies for BF_4^- have been found to be $\nu_1(1) = 772$ cm.$^{-1}$, $\nu_2(2) = 361$ cm.$^{-1}$, $\nu_3(3) = 1041$ cm.$^{-1}$ and $\nu_4(3) = 526$ cm.$^{-1}$. (These are the average values obtained from the individual values reported in the infrared and Raman studies.) The B–F interatomic distance can be taken as 1.43 ± 0.03 Å.[5-7] Therefore, the moment of inertia is $(172 \pm 8) \times 10^{-40}$ g. cm.^{2}. These data now can be used to calculate the thermodynamic functions for BF_4^-

The thermodynamic functions C_p° $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$ and S° have been calculated for the fluoborate ion, BF_4^-, in the temperature range from 200 to 1000°K. The rigid rotator-harmonic oscillator approximation has been used for the ideal gas at a pressure of one atmosphere. The values of the thermodynamic functions are listed in Table I.

Table I

Thermodynamic Functions for BF_4^- in the Ideal Gas State in Cal./Deg./Mole

T, °K.	Cp°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
200	12.74	9.37	49.13	58.50
250	14.69	10.24	51.30	61.55
298.16	16.33	11.10	53.18	64.28
300	16.39	11.13	53.25	64.38
400	19.03	12.79	56.68	69.48
500	20.83	14.23	59.70	73.93
600	22.05	15.44	62.41	77.85
700	22.90	16.45	64.86	81.31
800	23.50	17.29	67.12	84.41
900	23.95	18.01	69.19	87.20
1000	24.27	18.62	71.13	89.75

The uncertainties in $-(F^\circ - H_0^\circ)/T$ and S° due to the uncertainty in the moment of inertia amount to ±0.14 cal./deg./mole. The total uncertainties due to the uncertainty in the moment of inertia and in the vibrational frequencies are for C_p° about ±0.1 cal./deg./mole, for $-(F^\circ - H_0^\circ)/T$ from ±0.2 to ± 0.3 cal./deg./mole and for S° from ±0.3 to ±0.4 cal./deg./mole.

The thermodynamic functions for BF_3 have been calculated already.[8] Recently, the interatomic distance B–F in BF_3 has been redetermined as 1.295 Å. from an analysis of the vibrational–rotational fine structure.[9] The revised moments of inertia using this interatomic distance are 158.7×10^{-40} g.cm.^{2} and 79.34×10^{-40} g.cm.^{2}. The older moments of inertia were 157.7×10^{-40} g.cm.^{2} and 78.84×10^{-40} g.cm.^{2}.[2,8,10] The values of $-(F^\circ - H_0^\circ)/T$ and S° are increased by 0.019 cal./deg./mole by this revision in the moments of inertia of BF_3.

The entropy of the reaction

$$BF_3(g) + F^-(g) \longrightarrow BF_4^-(g) \qquad (1)$$

can be calculated. The entropy of $BF_3(g)$ at 25° is 60.72 e.u. and the entropy of $F^-(g)$ from the Sackur–Tetrode equation at 25° is 34.77 e.u. Since the entropy of BF_4^- at 25° from Table I is 64.28 e.u., the entropy of the reaction above is −31.21 e.u.

The contributions of the coulombic and repulsion interactions to the lattice energies of KBF_4 and NH_4BF_4 can be calculated from the Born equation.[11,12] The lattice constants for the high temperature cubic modifications of KBF_4 and NH_4BF_4 are available.[6] These salts at high temperatures crystallize in the NaCl type lattice (with free rotation of BF_4^- [6]) with minimum cation–anion distances for KBF_4 and NH_4BF_4 of 3.63 and 3.78 Å. The BF_4^- ion has 42 electrons,[4] consequently, it falls between the Kr and Xe electronic configurations. For KBF_4 a repulsion constant between those used for KBr and KI[12] seems reasonable, that is, about 10. For NH_4BF_4 a repulsion constant between NH_4Br and NH_4I[12] of 9 is used. The contributions from the coulombic and repulsion interactions to the total lattice energies now can be calculated from the Born equation to be 144 and 136 kcal./mole for KBF_4 and NH_4BF_4, respectively.

The contribution of the van der Waals interactions to the lattice energies of KBF_4 and NH_4BF_4 also can be evaluated approximately. The energy resulting from the dipole–dipole interactions, C/r_0^6, has been calculated by the method used by Mayer.[13] The value of C depends on the lattice type, the polarizabilities and the "main frequency" energies of the ions. The lattice type, NaCl cubic, and the polarizabilities and the "main frequency" energies of K^+ and NH_4^+ are available.[13-15] The polariza-

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bility of BF_4^- has been estimated previously as about 3 × 10^{-24} cm.^{3},[3,16] However, taking the refractive index, n_D, of KBF_4 as 1.32 ± 0.01[17] and using the method of Tessman, *et al.*,[14] a polarizability for BF_4^- of (4.85 ± 0.15) × 10^{-24} cm.^{3} can be obtained. The "main frequency" energy ϵ_- for BF_4^- is not available. However, it seems probable that it will lie somewhere near those of the halide ions.[13] An average value of (15 ± 5) × 10^{-12} ergs/mole is assumed for ϵ_- for BF_4^-. Using these data, the van der Waals energies for KBF_4 and NH_4BF_4 resulting from the dipole–dipole interactions are 6 and 7 kcal./mole, respectively. The energy contributions resulting from the dipole–quadrupole interactions[13] are taken as 0.2 C/r_0.[6] The total van der Waals energy terms for KBF_4 and NH_4BF_4 are about 8 and 9 kcal./mole, respectively.

The total lattice energies for KBF_4 and NH_4BF_4 (obtained by adding the contributions from the Born equation and the van der Waals energies) are 152 (at 300°) and 145 (at 260°) kcal./mole. The total uncertainties in the lattice energies resulting from the use of the Born equation, the approximate calculation of the van der Waals energy, and the approximation involved in the addition of the component energy terms are probably ±5 to 10 kcal./mole. Previously, a very approximate lattice energy calculation gave a lattice energy for KBF_4 of 148 kcal./mole.[16]

The lattice energy of KBF_4 can be combined with the heat of formation of KBF_4(s) and that of K^+(g) in the reaction $KBF_4(s) \rightarrow K^+(g) + BF_4^-(g)$ to obtain the heat of formation of the gaseous fluoborate ion. The heats of the dissociation reactions $MBF_4 \rightarrow MF + BF_3$ have been determined for the alkali metal fluoborates.[16] In the case of KBF_4 the dissociation reaction has been studied from below the m.p. of KBF_4 (530°) to 930°. The heat of dissociation is calculated to be 29 kcal./mole from the slope of the line in the plot of log *p versus* $1/T$.[16] Since no break occurs in the line at the m.p. of KBF_4, the heat of the reaction $KBF_4(s) \rightarrow KF(s) + BF_3(g)$ at 510° also is about 29 kcal./mole. The ΔH°_f(KF,s) at 510° is −128 kcal./mole,[18] while $\Delta H^\circ_f(BF_3,g)$ at 510° is −261 kcal./mole.[8,19] Consequently, the heat of formation of KBF_4(s) at 510° is −418 kcal./mole and at 25° is about −424 kcal./mole (assuming $H^\circ - H^\circ_0$ for KBF_4 is about the same as those of the alkali metal halides[18]). The heat of formation of BF_4^-(g) at 25° can be calculated to be −395 ± 10 kcal./mole from the reaction $KBF_4 \rightarrow K^+(g) + BF_4^-(g)$, since the heat of the reaction is the lattice energy of 152 kcal./mole (the change in lattice energy with temperature is negligible), $\Delta H^\circ_f(KBF_4,s)$ is −424 kcal./mole and $\Delta H^\circ_f(K^+,g)$ is 123 kcal./mole.[20]

The heat of reaction (1) at 25° is −62 ± 10 kcal./mole. This value is based on a $\Delta H^\circ_f(BF_3,g)$ at 25° of −268 kcal./mole[19] and a $\Delta H^\circ_f(F^-,g)$ at 25° of −65 kcal./mole.[20] Combining the heat of reaction (1), with its entropy gives a free energy of −53 ± 10 kcal./mole. The corresponding equilibrium constant at 25°, K_{eq}, has the value 10^{39}. Thus the reaction is spontaneous in the direction indicated above, and the equilibrium is very far over toward the formation of BF_4^-(g).

The heat of solution of KBF_4 in water is about 22 kcal./mole using approximate solubility data.[16] The $\Delta H^\circ_f(BF_4^-,aq)$ is −342 ± 10 kcal./mole, using $\Delta H^\circ_f(KBF_4,s)$ of −424 kcal./mole, $\Delta H_{soln.}$ of 22 kcal./mole and $\Delta H^\circ_f(K^+,aq)$ of −60.0 kcal./mole[20] in reaction (2)

$$KBF_4(s) \longrightarrow K^+(aq) + BF_4^-(aq) \qquad (2)$$

The heat of hydration of BF_4^- also can be calculated from the heats of formation of BF_4^-(g) of −395 kcal./mole and BF_4^-(aq) of −342 kcal./mole as about −54 kcal./mole ($\Delta H^\circ_f(H^+,aq)$ = +107 kcal./mole).[21]

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The Boron Trifluoride–Nitrogen Tetroxide Complex. Its Composition and Chemical Behavior

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When boron trifluoride and the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide are brought together in the vapor phase, the liquid phase, or in solution, heat is evolved and a stable, white, solid complex immediately separates. Mention is made of such a complex by Kuhlmann,[2] although he gives no data on its method of preparation, composition, analyses or properties. Batey and Sisler[3] mention a white, crystalline solid formed in the reaction of BF_3 with NO_2Cl containing N_2O_4 as an impurity, which they formulate as $N_2O_4 \cdot 2BF_3$. These authors also supply no other data on this complex.

Composition of the Complex.—Since we had expected for theoretical reasons that boron trifluoride and nitrogen tetroxide would form a complex of the type $BF_3 \cdot N_2O_4$ it was first decided to study the combining ratios of the two substances. This was done both gravimetrically and volumetrically. The results in both cases confirmed the expected composition.

Physical Properties of the Complex.—The white solid obtained by any of the various methods of mixing the component compounds is essentially insoluble in all solvents with which it does not react. Even nitromethane, nitrobenzene and liquid N_2O_4 do not dissolve it appreciably. It is also insoluble in aliphatic hydrocarbons and chlorinated hydrocarbons. It reacts with oxygenated solvents such as water, carboxylic acids, esters, ketones and

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