Greek Letters

γ = activity coefficient
δ = root mean squares deviation
Λ_{12}, Λ_{21} = Wilson parameters
π = pressure, mm. of Hg

Subscripts

1 = light component
2 = heavy component

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Enthalpy of Alkali Metal Fluoroborates from 298–1000° K

Enthalpies and Entropies of Fusion and Transition

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The enthalpies and entropies of $NaBF_4$, KBF_4, $RbBF_4$, and $CsBF_4$ have been measured from 298 to 1000° K with a copper block drop calorimeter. Their enthalpies of melting in kcal $mole^{-1}$ are 3.25, 4.30, 4.68, and 4.58, respectively, and enthalpies of transition are 1.61, 3.30, 2.86, and 1.94, respectively. The entropies of melting in cal deg^{-1} $mole^{-1}$ for the four salts are 4.78, 5.10, 5.5, and 5.5, respectively, while entropies of transition are 3.1, 5.9, 5.5, and 4.4, respectively. The transition behavior is discussed in terms of differences in structure and cation size.

Sodium fluoroborate is the main component of a proposed coolant mixture for a molten salt reactor. We have measured the high temperature enthalpies of $NaBF_4$, KBF_4, $RbBF_4$, and $CsBF_4$ to obtain information for reactor technology as well as to explore the interesting transition behavior of the solid fluoroborates. The melting points and solid transition temperatures, densities and molar volumes, and predicted volume changes on transition of the alkali fluoroborates have been reported (*3*). We now propose to examine the effect of the differences in structure and cation size on the enthalpy and entropy of fusion and transition in the alkali fluoroborates.

EXPERIMENTAL

The copper block drop calorimeter used for the measurements as well as the experimental procedure have been described in detail previously (*5*). Briefly, the experiment is performed by measuring the temperature rise of a copper block when an equilibrated encapsulated sample is dropped into a well in the block from the constant temperature zone of a controlled tube furnace. The enthalpy equivalent of the calorimeter relates the temperature rise of the block to the enthalpy of the sample and was determined with a NBS sample of synthetic sapphire using the same procedure as described above. The temperature of the sample was measured to ±0.1° with a calibrated platinum (90% platinum-10% rhodium) thermocouple. The temperature rise of the block was measured to ±0.001° with a calorimetric-type, platinum-sheathed platinum resistance thermometer. The salts were sealed in an inner platinum liner to prevent attack on the inconel capsules especially designed for our enthalpy apparatus. The enthalpy of the empty inconel capsules was measured in a separate series of experiments. The enthalpy of the platinum (*10*) amounted to only about 10 to 15% of that of the salt. Both the platinum and inconel capsules were welded closed in a helium drybox.

$NaBF_4$ and KBF_4 were prepared by recrystallization of commercial $NaBF_4$ and KBF_4 from dilute HF solutions. Further treatment of molten $NaBF_4$ at 425° C with a mixture of anhydrous HF, BF_3, and helium improved its purity. Sharp breaks in the DTA melting curves were obtained for $NaBF_4$ and KBF_4 at 406 and 569° C, respectively. $RbBF_4$ and $CsBF_4$ were prepared by the following reactions:

$$H_3BO_3(cr) + 4HF\ (58\%\ aq) = HBF_4(aq) + 3H_2O(l) \qquad (1)$$

$$MF(aq) + HBF_4(aq) = MBF_4(cr) + HF(aq) \qquad (2)$$

Table I. Measured Enthalpies

$NaBF_4$		KBF_4	
Temp, ° K	$H_T - H_{298}$, kcal $mole^{-1}$	Temp, ° K	$H_T - H_{298}$, kcal $mole^{-1}$
403.7	3.17	428.3	3.89
423.3	3.87	453.1	4.69
443.5	4.58	477.7	5.53
463.5	5.35	500.6	6.34
483.2	6.08	524.8	7.18
501.2	6.80	570.8	12.18
534.5	9.72	594.0	12.98
573.2	11.13	623.5	13.98
598.1	12.01	672.6	15.68
625.5	13.02	721.5	17.38
648.5	13.89	771.0	19.12
688.3	18.60	821.8	20.98
691.2	18.71	854.9	26.44
698.3	18.98	863.9	26.80
707.3	19.35	871.2	27.08
717.0	19.73	884.6	27.61
		896.3	28.10
$RbBF_4$		$CsBF_4$	
417.3	3.60	371.8	2.18
437.2	4.23	391.2	2.79
457.5	4.91	400.8	3.10
477.2	5.60	412.8	3.50
501.7	6.46	424.8	3.91
531.3	10.36	454.6	6.86
556.0	11.20	469.8	7.39
584.5	12.17	497.1	8.33
625.0	13.54	528.7	9.42
674.1	15.26	570.0	10.80
722.0	16.89	624.8	12.64
767.3	18.46	674.3	14.35
792.9	19.34	727.8	16.19
811.6	19.97	767.8	17.58
827.9	20.53	793.4	18.47
865.2	26.56	837.5	24.56
872.8	26.85	849.3	25.03
884.1	27.32	861.2	25.51
902.9	28.05	874.8	26.06
922.3	28.83	907.8	27.35
945.6	29.77	936.4	28.45

The precipitated MBF_4 (M is either Rb or Cs) was washed with cold water and dried in a 100° C oven. Sharp breaks in the DTA melting curves were obtained for $RbBF_4$ and $CsBF_4$ at 582° and 555° C, respectively. A more detailed description of the preparation, chemical analysis, and DTA melting curves for these compounds is given (*3*).

RESULTS AND DISCUSSION

The measured enthalpies are given in Table I. A computer program (*7*) was used to obtain the least-squares equations given in Table II and the smoothed values of enthalpy and entropy given in Table III. The program sets $\Delta H = 0$ at 298° K and fixes C_p at 298° K by an input parameter. Since no room temperature values of C_p have been reported, we estimated values for C_p at 298° K by extrapolation of our high temperature data. The data were fitted to the standard equation for heat content:

$$H_T - H_{298} = a + bT + cT^2 + dT^{-1} \qquad (3)$$

in the temperature region below the transition. For the temperature region between the transition and melting temperatures as well as for the regions above the melting temperature, the data were best fitted by a straight line equation. The fit of the data to the equations as shown in Table II is:

$$\text{av \% deviation} = \sum \frac{|\text{enthalpy}_{(\text{obsd})} - \text{enthalpy}_{(\text{calcd})}|}{\text{enthalpy}_{(\text{calcd})}} \times 100/n \qquad (4)$$

Details concerning the accuracy with which the primary variables and the calibration with Al_2O_3 were measured are given in (*5*). An overall accuracy of ±0.5% is estimated for the enthalpy measurements from a consideration of the measurement of the primary variables, calibration of the calorimeter, empty can enthalpy, purity of the compounds, and any small uncorrected systematic errors inherent in the method. An accuracy of ±1 to 2% is estimated for the enthalpies of fusion and transition. The somewhat larger error results from the fact that a difference between two larger measured numbers is involved in the calculation of the enthalpies of fusion and transition.

The measurements extended to only about 50 to 100° C above the melting points of the salts because of the rapidly increasing BF_3 dissociation pressure above these temperatures. Calculations based on the equilibrium vapor pressure measurements of Cantor (*2*) for the reaction $MBF_4 = MF + BF_3$ and the gas volume of the calorimeter capsule indicate that the fluoride concentration at the highest temperature of measurement was only about 0.05 mole %. A correction of less than 0.1% due to the vaporization of BF_3 would be extremely difficult to assess quantitatively and was not made, but instead it is included in the error in the accuracy reported above. Enthalpy and entropy values at 800 and 900° C in Table III for $NaBF_4$ are extrapolated and are included for comparison with those of the other fluoroborates in the liquid phase.

KBF_4, $RbBF_4$, and $CsBF_4$ all undergo a solid state transition from the $BaSO_4$ type orthorhombic structure to the high temperature cubic structure (*4, 6, 8*). $NaBF_4$, on the other hand, exists as the orthorhombic (pseudotetragonal) $CaSO_4$ type of structure (*1*) at room temperature, and in a noncubic form above the transition temperature (*6, 9*). This latter structure has recently been reported (*9*) to be monoclinic with four molecules per unit cell. However, a lowering of the symmetry at higher temperature without a lowering of the number of molecules per unit cell is quite unlikely. The structure was derived from a powder pattern and the authors state that their assignment is not necessarily correct or unique. This inconsistency may be avoided by showing that the x-ray spacings [Table 2 (*9*)] are compatible with the assumption of a mechanical mixture of the orthorhombic, low-temperature phase with a high-temperature phase of hexagonal, rather than monoclinic, structure.

Although the entropies of fusion of $NaBF_4$ and KBF_4 are similar (Table IV), the entropy of transition of KBF_4 is much larger than that of $NaBF_4$ (5.93 eu to 3.13 eu). This may be explained qualitatively on the basis of the differing structures of both the low and high-temperature solids which in turn are due to the large difference in the size of the cations. The $NaBF_4$ structure attains more disorder between 298° K and the transition which is reflected by the fact that at 500° K, $S_T - S_{298}$ is more than 1 eu larger for $NaBF_4$ than for KBF_4. In addition, the high temperature cubic structure of KBF_4 most probably is more compatible with anionic rotational or librational disorder than is the structure of $NaBF_4$ of lower symmetry. However, the considerable figure of about 3 eu for the entropy of transition of $NaBF_4$ suggests that the noncubic high temperature form of this compound also exhibits some anionic rotational disorder.

KBF_4, $RbBF_4$, and $CsBF_4$ are isodimorphous (*4*) and therefore can be considered as a series separate from $NaBF_4$. Although the enthalpies and temperatures of melting are similar (Table IV), there is a total decrease in temperature, entropy, and enthalpy of transition in this series of 20, 25, and 41% respectively, with increasing cation size. The particularly large relative change in the enthalpy may be

Table II. Equation Coefficients for Enthalpy Data for Equation: $H_T - H_{298}$ (Kcal Mole^{-1}) $= a + bT + cT^2 + dT^{-1}$

Compound	$a \times 10^{-3}$	b	$c \times 10^2$	$d \times 10^{-4}$	Av Dev, %	Temp Range, °K
$NaBF_4$	−3.820	3.148	3.703	−12.17	0.3	298–516
	−9.785	36.48	. . .	. . .	0.1	516–679
	−8.605	39.52	. . .	. . .	0.1	679–750
KBF_4	−6.325	15.62	1.943	−1.737	0.2	298–556
	−7.800	34.95	. . .	. . .	0.2	556–843
	−7.710	39.94	. . .	. . .	0.1	843–900
$RbBF_4$	−7.430	18.77	1.697	+9.677	0.2	298–518
	−7.897	34.34	. . .	. . .	0.1	518–855
	−7.985	39.92	. . .	. . .	0.1	855–1000
$CsBF_4$	−7.614	17.63	2.009	+17.01	0.2	298–443
	−8.673	34.18	. . .	. . .	0.1	443–828
	−8.390	39.36	. . .	. . .	0.1	828–1000

Table III. Smoothed Values of Enthalpy and Entropy

	$NaBF_4$			KBF_4	
Temp, °K	$H_T - H_{298}$, kcal mole^{-1}	$S_T - S_{298}$, cal deg^{-1} mole^{-1}	Temp, °K	$H_T - H_{298}$, kcal mole^{-1}	$S_T - S_{298}$, cal deg^{-1} mole^{-1}
298	0	0	298	0	0
400	3.06	8.77	400	2.99	8.59
500	6.76	17.01	500	6.31	15.98
516	7.43	18.31 (orthorhombic $CaSO_4$)	556	8.33	19.82 (orthorhombic $BaSO_4$)
516	9.04	21.44 (hexagonal?)	556	11.63	25.75 (cubic)
600	12.10	26.94	600	13.17	28.42
679	14.98	31.45 (hexagonal?)	700	16.67	33.80
679	18.23	36.23 (liquid)	800	20.16	38.47
700	19.06	37.43	843	21.66	40.30 (cubic)
800	(23.01)[a]	(42.71)[a]	843	25.96	45.40 (liquid)
900	(26.96)[a]	(47.36)[a]	900	28.24	48.01
	$RbBF_4$			$CsBF_4$	
298	0	0	298	0	0
400	3.04	8.73	400	3.08	8.85
500	6.39	16.20	443	4.51	12.24 (orthorhombic $BaSO_4$)
518	7.03	17.47 (orthorhombic) $BaSO_4$	443	6.45	16.63 (cubic)
518	9.89	22.98 (cubic)	500	8.42	20.81
600	12.71	28.03	600	11.83	27.04
700	16.14	33.32	700	15.25	32.31
800	19.57	37.91	800	18.67	36.87
855	21.46	40.19 (cubic)	828	19.63	38.05 (cubic)
855	26.15	45.67 (liquid)	828	24.20	43.57 (liquid)
900	27.94	47.74	900	27.03	46.85
1000	31.94	51.92	1000	30.97	51.00

[a] Extrapolated

Table IV. Enthalpies and Entropies of Melting and Transition of Alkali Metal Fluoroborates

	T_m, °K	ΔH_m, kcal mole^{-1}	ΔS_m, eu mole^{-1}	T_{tr}, °K	ΔH_{tr}, kcal mole^{-1}	ΔS_{tr}, eu mole^{-1}	$\Delta S_m + \Delta S_{tr}$, eu mole^{-1}
$NaBF_4$	679	3.25	4.78	516	1.61	3.1	7.9
KBF_4	843	4.30	5.10	556	3.30	5.9	11.0
$RbBF_4$	855	4.68	5.5	518	2.86	5.5	11.0
$CsBF_4$	828	4.58	5.5	443	1.94	4.4	9.9

attributed to the decrease in lattice energy with increasing size of the cation. The relatively low temperature of transition found for $CsBF_4$ follows from the large decrease in enthalpy as compared to the entropy of transition.

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