# Enthalpy of Lithium Fluoroborate from 298–700K

## Enthalpy and Entropy of Fusion

ARTHUR S. DWORKIN
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830

**The enthalpy and entropy of $LiBF_4$ have been measured from 298–700K with a copper block drop calorimeter. The enthalpy and entropy of melting of $LiBF_4$ are 3460 cal $mol^{-1}$ and 5.94 cal $deg^{-1}$ $mol^{-1}$, respectively. No evidence for a transition between room temperature and the melting point was found. The results are compared with those for the other alkali metal fluoroborates.**

We have examined the effect of the differences in structure and cation size on the enthalpy and entropy of fusion and transition in the alkali fluoroborates sodium through cesium (*4*). Lithium fluoroborate with its much smaller cation differs from the other fluoroborates in that it has at room temperatures a hexagonal structure type, probably that of $SiO_2$ (*1*). A recent paper (*2*) reports that there is no transition in $LiBF_4$ between room temperature and the melting point while another (*6*) reports a transition at 115°C. We, therefore, have measured the enthalpy of $LiBF_4$ from room temperature up to about 40°C above its melting temperature to complete our thermochemical studies of the alkali metal fluoroborates.

## EXPERIMENTAL

The copper block drop calorimeter used for the measurements and 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°C with a calibrated platinum (90% platinum–10% rhodium) thermocouple. The temperature rise of the block was measured to ±0.001°C with a calorimetric-type, platinum-sheathed platinum resistance thermometer. The $LiBF_4$ was sealed in an inner platinum liner to prevent attack on the Inconel capsule especially designed for our enthalpy apparatus. The enthalpy of the empty Inconel capsule was measured in a separate series of experiments. The enthalpy of the platinum (*7*) amounted to only about 15% of that of the salt. Both the platinum and Inconel capsules were welded closed in a helium dry box.

A thermal analysis was performed to determine the melting point of $LiBF_4$ as well as to examine the possible transition behavior. For this experiment, the $LiBF_4$ was sealed in a nickel capsule in the same manner as above. The capsule was mounted in an enclosed argon-filled stainless steel tube in a Nichrome-wound Marshall furnace. Temperatures were measured with a Pt(Pt–10% Rh) thermocouple placed in a well extending about 1.5 cm into the capsule from the bottom. The signal from the couple was fed into a Rubicon potentiometer and then into a Brown recorder with a chart span of 1 mV thus permitting temperature-time curves to be recorded during the heating and cooling cycles.

The $LiBF_4$, purchased from Foote Mineral Co., was prepared in an anhydrous solvent and never came into contact with air; the salt was always transferred in a dry box filled with helium. It was also subjected to a dynamic vacuum at room temperature for 24 hr before encapsulation. The only appreciable impurity was LiF. A chemical analysis performed in the ORNL Analytical Chemistry Division showed that our sample contained 3 mol % LiF. The analytical method entails a titration with thorium nitrate solution performed immediately after sample dissolution. The indicator used is methyl thymol blue with the pH of the solution adjusted to 3.35. The $BF_4^-$ ion is hydrolyzed so slowly in cold water (*8*) that the degree of hydrolysis during the time of analysis is immeasurable within the accuracy of the titration (better than ±2%). The indicated free fluoride, therefore, comes almost entirely from excess LiF.

## RESULTS AND DISCUSSION

The measured enthalpies corrected for the contribution of the enthalpy of LiF (*3*) are given in Table I. The correction amounted to about 0.5% for enthalpies below the melting point and about 1.5% for those above. The following least-

**Table I. Measured Enthalpies of $LiBF_4$**

(Corrected for LiF impurity)

| Temp, K | $H_T - H_{298}$, kcal $mol^{-1}$ | Temp, K | $H_T - H_{298}$, kcal $mol^{-1}$ |
|---|---|---|---|
| 364.0 | 1.82 | 550.8 | 7.47 |
| 391.4 | 2.60 | 588.0 | 12.07 |
| 421.2 | 3.44 | 590.9 | 12.22 |
| 452.5 | 4.40 | 594.3 | 12.37 |
| 482.2 | 5.27 | 598.6 | 12.54 |
| 512.7 | 6.25 | 605.4 | 12.78 |
| 536.8 | 7.02 | 611.1 | 13.02 |

**Table II. Smoothed Values of Enthalpy and Entropy of $LiBF_4$**

| Temp, K | $H_T - H_{298}$, kcal $mol^{-1}$ | $S_T - S_{298}$, cal $deg^{-1}$ $mol^{-1}$ |
|---|---|---|
| 298 | 0 | 0 |
| 350 | 1.41 | 4.37 |
| 400 | 2.85 | 8.20 |
| 450 | 4.33 | 11.70 |
| 500 | 5.85 | 14.90 |
| 550 | 7.40 | 17.85 |
| 583 | 8.43 | 19.67 (solid) |
| 583 | 11.89 | 25.61 (liquid) |
| 600 | 12.58 | 26.76 |
| 650 | 14.58 | 29.97 |
| 700 | 16.59 | 32.95 |

**Table III. Enthalpies and Entropies of Melting and Transition of Alkali Metal Fluoroborates**

|  | $T_m$, K | $\Delta H_m$, kcal mol$^{-1}$ | $\Delta S_m$, cal deg$^{-1}$ mol$^{-1}$ | $T_{tr}$, K | $\Delta H_{tr}$, kcal mol$^{-1}$ | $\Delta S_{tr}$, cal deg$^{-1}$ mol$^{-1}$ | $\Delta S_m + \Delta S_{tr}$, cal deg$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $LiBF_4$ | 583 | 3.46 | 5.94 | ... | ... | ... | 5.9 |
| $NaBF_4$ | 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 |

squares equations represent the corrected enthalpy data for $LiBF_4$ in cal mol$^{-1}$:

$$H_T - H_{298} = -11{,}440 + 31.89\,T + 1.0 \times 10^{-8}\,T^2 + 5.50 \times 10^5\,T^{-1} \text{ (298–583K)}$$

$$\Delta H_{\text{fusion}} = 3460 \text{ cal mol}^{-1}; \; \Delta S_{\text{fusion}} = 5.94 \text{ cal deg}^{-1} \text{ mol}^{-1} \text{ (583K)}$$

$$H_T - H_{298} = -11{,}490 + 40.1\,T \text{ (583–700K)}$$

A computer program was used to obtain the least-squares equations given above and the smoothed values of enthalpy and entropy given in Table II. The program sets $\Delta H = 0$ at 298K and fixes $C_p$ at 298K 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 average % deviation of the data from the equations,

$$\left(\sum \frac{{}^*\text{enthalpy}_{\text{obsd}} - \text{enthalpy}_{\text{calcd}}{}^*}{\text{enthalpy}_{\text{calcd}}} \times 100/n\right)$$

is 0.4% in the solid and 0.1% in the liquid. An overall accuracy of ±0.8% is estimated for the enthalpy measurements and an accuracy of ±1-2% is estimated for the enthalpy of fusion.

We found no evidence for a transition either in the enthalpy measurements or in a separate thermal analysis experiment. $LiBF_4$ is hygroscopic and must be handled in a dry inert atmosphere as it was in our work and in that of ref. *2*. However, this was not the case in the work reported in ref. *6* where, in fact, the $LiBF_4$ was ground to a fine powder in the open and heated in an open system for their differential thermal analysis experiments. Our thermal analysis experiment showed two breaks at 304° and 300°C. The breaks most probably indicate the $LiBF_4$ liquidus and the eutectic in the $LiBF_4$–LiF system. From the liquidus temperature, the mol % LiF impurity, and the heat of fusion of $LiBF_4$, the true temperature of fusion is calculated to be 310°C. The eutectic concentration can also be estimated to be ~5 mol % LiF.

Table III compares the enthalpies and entropies of fusion and transition for the alkali metal fluoroborates. The high-temperature forms of the fluoroborates of sodium through cesium acquire considerable entropy at the transition temperature probably due to anionic rotational or librational disorder (*4*). Their entropy of melting, therefore, is lower than that for $LiBF_4$ although the sum of the entropy of transition and melting ($\Delta S_m + \Delta S_{tr}$) is higher than that for $LiBF_4$. $NaBF_4$ differs in both high- and low-temperature structure from the other fluoroborates (*4*) as well as from $LiBF_4$. This is reflected in its intermediate value for $\Delta S_m + \Delta S_{tr}$.

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