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The Enthalpies of Fusion of Li_2BeF_4, $LiBeF_3$, and Na_2BeF_4, and the Heat Capacities of the Liquid Mixtures

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As a part of an extended investigation of the thermochemistry of liquid and solid compounds in $AX–BX_2$ and $AX–CX_3$ systems, the heat capacities of solid and liquid Li_2BeF_4 and Na_2BeF_4, and of a liquid mixture of the $LiBeF_3$-composition have been measured. Furthermore, the enthalpies of fusion of the congruently melting compounds Li_2BeF_4 and Na_2BeF_4 have been determined. The following molar enthalpies of fusion were obtained in the temperature range investigated:

$$Li_2BeF_4: \Delta H_f = -336 + 14.06\ T \text{ cal mol}^{-1}$$
$$Na_2BeF_4: \Delta H_f = -9735 + 18.32\ T \text{ cal mol}^{-1}$$

The stability of the two solid compounds Li_2BeF_4 and $LiBeF_3$ has been discussed on the basis of data originally given by Holm and Kleppa and the heat capacities and enthalpies of fusion obtained in this work.

In the course of an extended investigation of the thermochemistry of liquid and solid metal halide mixtures, the enthalpies of fusion of some 2:1 and 1:1 compounds of alkali fluorides (LiF and NaF) and beryllium fluoride have been determined by means of a high precision drop calorimeter with adiabatic shields. With this calorimeter rather precise values for the heat capacities for the molten salt mixtures can also be obtained, as has been shown in a recent paper on alkali chloride-magnesium chloride mixtures by Holm *et al.*[1]

The thermodynamic properties as well as the structures of molten alkali fluoride-beryllium fluoride mixtures have for some time attracted the attention of several investigators. The enthalpy of mixing of liquid LiF-BeF_2, KF-BeF_2, and RbF-BeF_2 mixtures has been measured by Holm and Kleppa.[2] They suggested from the obtained ΔH^M-data that BeF_4^{2-} is an important anionic species in these mixed systems, particularly in the systems KF-BeF_2 and RbF-BeF_2, and to a lesser extent also in the system LiF-BeF_2.

Another contribution in the same field has been made by Braunstein *et al.*,[3] who calculated partial excess Gibbs free energies of AlkF in AlkF-BeF_2 mixtures from phase diagram data, and correlated their data with the chemical potential interaction parameter in charge-unsymmetrical mixtures. Raman spectra of BeF_4^{2-} in a molten LiF-NaF mixture has been reported by Quist *et al.*[4] They kept the BeF_2 content constant at 33 mol %, and were therefore unable to report upon any change in the spectra with composition. They concluded, however, that strong $Be^{2+} - F^-$ interactions are present in these mixtures, and also that Be^{2+} is tetrahedrally surrounded by F^- ions.

The phase diagram of the system LiF-BeF_2, and the phase equilibria in this system, have recently been reinvestigated by Romberger *et al.*,[5] who for the first time established Li_2BeF_4 as a congruently melting compound with a phenacite (Be_2SiO_4)-type structure. This system also contains the compound $LiBeF_3$, which disproportionates in the solid state at 290°C to Li_2BeF_4 and BeF_2.

The system NaF-BeF_2 contains a congruently melting compound corresponding to Na_2BeF_4, as shown in the phase diagram by Roy *et al.*[6]

In the paper by Holm *et al.*[1] the possible formation and stability of complex ions in the binary systems KCl-$MgCl_2$, RbCl-$MgCl_2$, and CsCl-$MgCl_2$ were discussed on the basis of the heat capacities of the liquid mixtures, and the enthalpies of mixing between the compounds. It was stressed that complex formation should not be considered as a *static* phenomenon in these systems. The results were rather indicative of changes in the stability of the complex ions as the temperature is varied. In this work the same methods will be used to elucidate the stability of the BeF_4^{2-} ion in molten lithium fluoride and sodium fluoride.

EXPERIMENTAL

A. Chemicals. Lithium fluoride (LiF, Fisher Certified Reagent) and sodium fluoride (NaF, *p.a.* from E. Merck, Germany) were melted in platinum crucibles in an atmosphere of purified nitrogen. Only clear crystals were selected from the samples. Beryllium fluoride (BeF_2, from the Brush Beryllium Co., USA) was a high purity product, which, according to the manufacturer, contains 99.5 % BeF_2.

For the preparation of Li_2BeF_4, $LiBeF_3$, and Na_2BeF_4 stoichiometric amounts of the alkali fluoride and beryllium fluoride were melted together in a platinum crucible in a purified nitrogen atmosphere.

B. Calorimetry. Duplicate samples of each of the compounds were loaded into platinum containers of known mass. The containers were evacuated carefully inside a glove box to get rid of the air. The glove-box was filled with purified nitrogen. After evacuation, the containers were filled with purified argon. They were then sealed by arc-welding a cup-shaped platinum lid to the rim of the container.

The sample was equilibrated in a vertical laboratory furnace and lifted into the silver calorimeter, which was placed above the furnace. The calorimeter was surrounded by silver shields, electrically heated to maintain quasi-adiabatic conditions. The furnace temperature was measured by a quartz thermometer. Temperatures are in terms of the International Practical Temperature Scale of 1968. The calorimeter proper, the calibration of the calorimeter, and the method of calculating the enthalpy increments $H_T - H_{298.15}$ have been described in detail by Grønvold.[7]

Steady state conditions were usually obtained after 10 – 20 min, depending on the furnace temperature. The calorimeter temperature during the period of experiments ranged from 298 to 330 K with a mean of 315 K. The heat capacity values for the compounds were estimated from those for the binary compounds by the relationship

$$c_p = nC_p(\mathrm{AlkF}) + C_p(\mathrm{BeF_2}),\ (n = 1 \text{ or } 2) \quad (1)$$

The heat capacity values at 315 K, used for adjusting the enthalpies to 298 K, are listed in Table 1.

Table 1. Heat capacity values at 315 K (from JANAF [8]).

Compound	C_p/cal K^{-1} mol^{-1}
LiF	10.19
NaF	11.31
BeF_2	12.70
Li_2BeF_4	33.08
$LiBeF_3$	22.89
Na_2BeF_4	35.26

RESULTS

(a) *Na_2BeF_4*. The enthalpy increments are listed in Tables 2 and 3 and plotted in Fig. 1. From our data we obtain the following relations (σ is the standard deviation)

Na_2BeF_4(s):

$$H_T - H_{298.15} = -10986 + 44.68\ T \text{ cal} \quad (\sigma = 185) \quad (2)$$

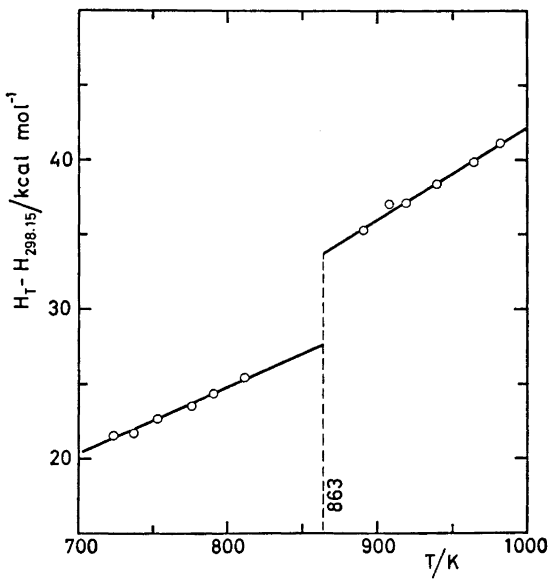

Fig. 1. Enthalpy curve, $H_T - H_{298.15}$ for Na_2BeF_4, this work.

Table 2. Experimental and calculated enthalpy increments for solid Li_2BeF_4 and Na_2BeF_4.

T/K	$\frac{H_T - H_{298.15}}{\text{cal mol}^{-1}}$ exp.	calc.
	Li_2BeF_4	
572.8	10539	10555
601.5	12009	11921
625.1	13024	13043
650.1	14075	14233
677.1	15549	15518
693.0	16451	16274
707.0	16837	16940
	Na_2BeF_4	
724.2	21615	21373
737.3	21777	21958
753.3	22632	22673
776.7	23554	23718
790.2	24339	24322
811.5	25400	25273

Table 3. Experimental and calculated enthalpy increments for liquid Li_2BeF_4, $LiBeF_3$, and Na_2BeF_4.

T/K	$\frac{H_T - H_{298.15}}{\text{cal mol}^{-1}}$ exp.	calc.
	Li_2BeF_4	
758.2	29200	29703
771.8	30427	30541
781.1	31413	31115
788.7	31924	31583
797.0	32326	32095
803.2	32216	32477
811.4	33051	32982
822.5	33767	33667
831.9	34519	34246
840.9	34593	34801
873.0	36554	36780
	$LiBeF_3$	
704.1	17044	17169
724.8	18177	18025
747.9	18962	18991
757.4	19458	19374
777.5	20113	20206
	Na_2BeF_4	
891.2	35269	35424
908.5	36999	36514
919.5	37020	37207
940.4	38346	38524
963.5	39833	39979
980.5	41232	41950

Na_2BeF_4(l):

$$H_T - H_{298.15} = -20721 + 63.00\ T \text{ cal} \quad (\sigma = 200) \tag{3}$$

This gives an equation for the enthalpy of fusion of Na_2BeF_4:

$$\Delta H_f(Na_2BeF_4) = -9735 + 18.32\ T \text{ cal mol}^{-1} \tag{4}$$

The enthalpy of fusion of Na_2BeF_4 at the melting point, 863 K, is 6.1 ± 0.2 kcal mol^{-1}. Values for this compound have not been reported in the literature.

(b) *Li_2BeF_4 and $LiBeF_3$.* The obtained enthalpy increments for these two compounds are listed in Tables 2 and 3 and plotted in Fig. 2. For lithium tetrafluoroberyllate we obtain the following results:

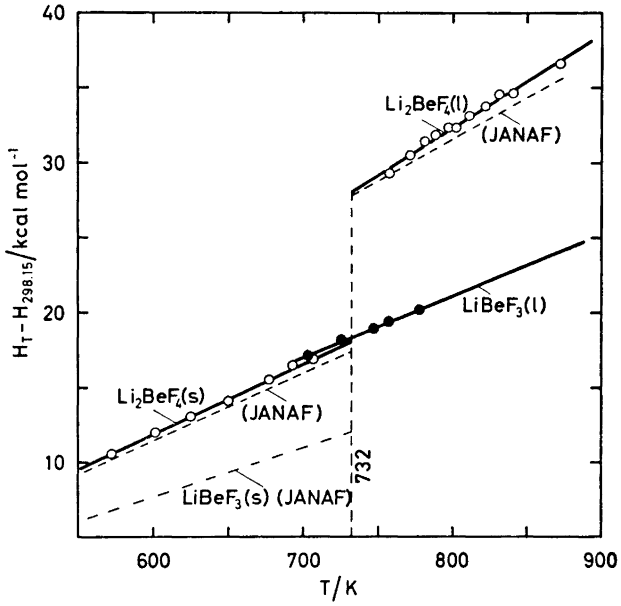

Fig. 2. Enthalpy curve, $H_T - H_{298.15}$ for Li_2BeF_4 and $LiBeF_3$. ○, Li_2BeF_4, this work; ●, $LiBeF_3$(l), this work; dotted line, Li_2BeF_4, data from JANAF;[8] dash-dotted line, $LiBeF_3$(s), data from JANAF.[8]

Li_2BeF_4(s):

$$H_T - H_{298.15} = -16698 + 47.58\ T \text{ cal} \quad (\sigma = 124) \tag{5}$$

Li_2BeF_4(l):

$$H_T - H_{298.15} = -17034 + 61.64\ T \text{ cal} \quad (\sigma = 194) \tag{6}$$

For liquid $LiBeF_3$ we find:

$LiBeF_3$(l):

$$H_T - H_{298.15} = -11965 + 41.38\ T \text{ cal} \quad (\sigma = 135) \tag{7}$$

On the basis of eqns. (5) and (6) we derive for the enthalpy of fusion of Li_2BeF_4:

$$\Delta H_f(Li_2BeF_4) = -336 + 14.06\ T \text{ cal mol}^{-1} \quad (8)$$

At the melting point 723.1 K this corresponds to $\Delta H_f = 10.0 \pm 0.15$ kcal mol^{-1}. This value should be compared with that given in JANAF,[8] $\Delta H_f = 10.6$ kcal mol^{-1}, which is based on the enthalpy determinations by Douglas and Payne.[9]

DISCUSSION

(a) *Enthalpy cycle calculations.* In the first part of the discussion we wish to demonstrate the use of two enthalpy cycles in calculations of enthalpy of reactions, since enthalpy of fusion and enthalpy of mixing data are available.

Cycle I at 732 K:

$$\begin{array}{ccccc} 2LiF(s) & + & BeF_2(s) & \xrightarrow{\Delta H_1} & Li_2BeF_4(s) \\ \downarrow 2\Delta H_f(LiF) & & \downarrow \Delta H_f(BeF_2) & & \downarrow \Delta H_f(Li_2BeF_4) \\ 2LiF(l) & + & BeF_2(l) & \xrightarrow{\Delta H_1^M} & Li_2BeF_4(l) \end{array}$$

According to the cycle

$$\Delta H_1^M = \Delta H_1 + \Delta H_f(Li_2BeF_4) - 2\Delta H_f(LiF) - \Delta H_f(BeF_2) \quad (9)$$

By inserting

$\Delta H_1 = -4.0$ kcal (Gross,[10] JANAF [8])
$\Delta H_f(Li_2BeF_4) = 10.0$ kcal mol^{-1} (this work)
$\Delta H_f(LiF) = 5.9$ kcal mol^{-1} (JANAF [8] and Douglas and Dever [11])
$\Delta H_f(BeF_2) = 1.2$ kcal mol^{-1} (JANAF [8] and Holm and Kleppa [2])

one finds

$$\Delta H_1^M(732\text{ K}) = -4.0 + 10.0 - 11.8 - 1.2$$
$$= -7.0 \text{ kcal (mol } Li_2BeF_4)^{-1}$$

This calculated value might be compared with the experimental enthalpy of mixing found by Holm and Kleppa [2] at 1135 K for the composition $X_{BeF_2} = 0.33$, $\Delta H^M = -1070$ cal (mol mixture)$^{-1}$. For the reaction

$$2LiF(l) + BeF_2(l) = Li_2BeF_4(l)$$

one therefore has

$$\Delta H_1^M(1135\text{ K}) = -3.2 \text{ kcal mol}^{-1}$$

This clearly shows the large temperature dependence of the enthalpy of mixing. The change in ΔH^M from 730 to 1135 K corresponds to an average change in the heat capacity of mixing of

$$\Delta C_p^M = \frac{-3200 + 7000}{400} = 9.5 \text{ cal K}^{-1} \text{ mol}^{-1}$$

This shows a very good agreement with the experimental value found in this work at 732 K:

$$\Delta C_p^M = 3.1 \text{ cal K}^{-1} \text{ (mol mixture)}^{-1} \text{ (Table 4)}$$

or

$$\Delta C_p^M = 9.3 \text{ cal K}^{-1} \text{ (mol } Li_2BeF_4)^{-1}$$

Cycle II at 732 K:

$$\begin{array}{ccccc} LiF(s) & + & BeF_2(s) & \xrightarrow{\Delta H_2} & LiBeF_3(s) \\ \downarrow \Delta H_f(LiF) & & \downarrow \Delta H_f(BeF_2) & & \downarrow \Delta H_f(LiBeF_3) \\ LiF(l) & + & BeF_2(l) & \xrightarrow{\Delta H_2^M} & LiBeF_3(l) \end{array}$$

According to cycle II

$$\Delta H_2 = \Delta H_f(LiF) + \Delta H_f(BeF_2) - \Delta H_f(LiBeF_3) + \Delta H_2^M \quad (10)$$

By inserting the values

$\Delta H_f(LiF) = 5.9$ kcal mol^{-1} (JANAF [8] and Douglas and Dever [11])
$\Delta H_f(BeF_2) = 1.2$ kcal mol^{-1} (JANAF [8] and Holm and Kleppa [2])
$\Delta H_f(LiBeF_3) = 6.3$ kcal mol^{-1} (this work)

one finds

$$\Delta H_2 = 0.8 + \Delta H_2^M \quad (11)$$

The enthalpy of mixing, ΔH_2^M, can be calculated from the enthalpies of mixing given by Holm and Kleppa.[2] For the 50:50 composition they found $\Delta H^M = -280$ cal (mol mixture)$^{-1}$ at 1135 K. By use of the calculated ΔC_p^M for this composition, $\Delta C_p^M = 4.8$ cal K^{-1} (mol $LiBeF_3)^{-1}$, it is possible to calculate the enthalpy of the reaction between liquid LiF and BeF_2 at 732 K:

$$LiF(l) + BeF_2(l) = LiBeF_3(l)$$

$$\Delta H_2^M(732 \text{ K}) = (-560 - 403 \times 4.8) = -2.5 \text{ kcal mol}^{-1}$$

Using this value in eqn. (11) we obtain

$$\Delta H_2 = -1.7 \text{ kcal mol}^{-1}$$

This value is in good agreement with the value reported by Gross [10] (see JANAF [8]) for reaction (II) at 298.15 K

$$LiF(s) + BeF_2(s) = LiBeF_3(s)$$

which is $= -1.8$ kcal mol^{-1}.

(b) *The heat capacities of the mixture.* From the slope of the enthalpy increment curves we find the heat capacities of the solids as well as of the liquids. From the heat capacities of the pure liquids we have calculated the changes in the heat capacity on mixing for some compositions. The results are summarized in Table 4. In the calculations we have used the following heat capacities:

LiF: 15.5 cal K^{-1} mol^{-1}, NaF: 16.4 cal K^{-1} mol^{-1} and
BeF_2: 17.9 at 700 K and 21.0 cal K^{-1} mol^{-1} at 1100 K (JANAF [8]).

The obtained heat capacities of mixing indicate that the BeF_4^{2-} ion is subject to dissociation in the LiF-BeF_2 melt as well as in the NaF-BeF_2 melt as the temperature increases. The BeF_3^- ion does not seem to be a pre-

Table 4. Changes in heat capacity on mixing x AlkF(l) + $(1-x)$$BeF_2$(l).

x	Alk	C_p/cal K^{-1} mol^{-1} comp.[a]	mix.	ΔC_p^M/cal K^{-1} mol^{-1} mix. − comp.	Temp. range K
0.67	Li	16.3 − 17.4	20.5	+4.2 − +3.1	700 − 1100
0.67	Na	16.6 − 17.7	21.0	+4.4 − +3.3	700 − 1100
0.50	Li	16.6 − 18.3	20.7	+4.1 − +2.4	700 − 1100

[a] As the heat capacity of liquid BeF_2 changes considerably with temperature, the C_p (comp.) and the C_p^M values will not be constant.

ferred complex ion in the melt in the actual temperature range, T above 1000 K. This can be seen from the fact that ΔC_p^M is about the same for the two mixtures 2/3 LiF + 1/3 BeF_2 and 1/2 LiF + 1/2 BeF_2. We therefore suggest that the most probable dissociation reaction for the tetrafluoro beryllate ion will be given as

$$BeF_4^{2-}{}_{(l)} = \text{“}BeF_2\text{”}_{(l)} + 2F^-{}_{(l)}$$

where “BeF_2“ denotes the inner and stable part (the non-polarizable part) of the complex.

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