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THERMOCHEMISTRY OF MOLTEN CRYOLITE MIXTURES

III. THE ENTHALPY OF FUSION AND CRYOSCOPY IN THE MOLTEN EUTECTIC MIXTURE $0.218Na_3AlF_6+0.782NaF$

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ABSTRACT

The enthalpy of fusion at the melting point of the eutectic mixture 0.218 $Na_3AlF_6+0.782$ NaF, 1162 K, has been determined by drop calorimetry and found to be 9086 ± 100 cal mol^{-1}. The possibility of evaluating so-called "entropy models" on the basis of cryoscopy data for this eutectic melt with small additions of Al_2O_3 (1–2 mol%) is discussed. It is shown that if the enthalpy term in the equation

$$\frac{\bar{H}_1}{T} - \bar{S}_1 = -\Delta H_f\left(\frac{1}{T} - \frac{1}{T_f}\right)$$

is neglected, such evaluations will lead to erroneous results.

INTRODUCTION

In the literature one frequently finds eqn (1)

$$\bar{S}_1 = -\frac{\bar{G}_1}{T} + \frac{\bar{H}_1}{T} \tag{1}$$

or

$$\bar{S}_1 = \Delta H_f\left(\frac{1}{T} - \frac{1}{T_f}\right) + \frac{\bar{H}_1}{T} \tag{2}$$

used to calculate partial entropies of mixing directly from freezing point depression data. These calculated entropies are then compared with theoretical values calculated from "entropy models" by using the "ideal" entropy equation

$$\bar{S}_1 = -R \ln N_1 \tag{3}$$

where N_1 denotes the mol fraction. Due to the lack of reliable enthalpy data, one often simply sets $\bar{H}_1 = 0$, using eqn (2) in the form

$$\bar{S}_1 = \Delta H_f\left(\frac{1}{T} - \frac{1}{T_f}\right) \tag{4}$$

thereby omitting the most interesting and the most important contribution, namely the enthalpy of mixing. In this paper it is shown that in mixtures of Na_3AlF_6, NaF, and Al_2O_3, the enthalpy of mixing term is too large to be neglected in accurate calculations.

RESULTS AND DISCUSSION

The revised phase diagram of the system NaF–AlF_3 has been given by Holm[1]. The enthalpy of fusion of the eutectic mixture 0.218 Na_3AlF_6+0.782 NaF at 889 °C has been determined by drop calorimetry. The drop experiments were carried out as described previously[2,3]. The results from the drop experiments are given in Table 1 and plotted in Fig. 1.

TABLE 1

EXPERIMENTAL AND CALCULATED ENTHALPY INCREMENTS FOR THE SOLID AND LIQUID MIXTURE 0.218 Na_3AlF_6+0.782 NaF

T/K	$\Delta H_T - H_{298.15}$/*cal*	
	Exp.	*Calc.*
1049.1	16747	16750
1072.0	17284	17291
1101.1	17998	17980
1122.8	18503	18493
1133.9	18738	18756
1155.1	21020	
1165.2	27531	
1196.7	29543	29555
1215.0	30130	30112
1230.2	30581	30575
1249.9	31153	31174
1269.2	31770	31762

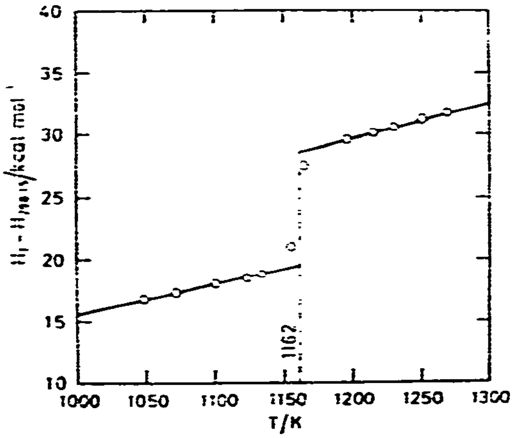

Fig. 1. Enthalpy increments $H_T - H_{298.15}$ and enthalpy of fusion of the eutectic mixture 21.8 mole % Na_3AlF_6+78.2 mol % NaF at 1162 K.

The data were fitted by a least squares treatment to equations of the type

$$H_T - H_{298.15} = a + b \cdot T \tag{5}$$

where b corresponds to the assumed constant heat capacity of the solid or the liquid. The following equations were obtained (σ is the calculated standard deviation):

solid mixture: $H_T - H_{298.15} = -8065 + 23.65T$ cal mol^{-1} ($\sigma = 16$)
liquid mixture: $H_T - H_{298.15} = -6881 + 30.45T$ cal mol^{-1} ($\sigma = 18$)

corresponding to an enthalpy of fusion of the mixture (0.218 Na_3AlF_6 + 0.782 NaF)

$$\Delta H_f = 1184 + 6.80T \text{ cal mol}^{-1} \tag{6}$$

with an estimated uncertainty of ± 100 cal mol^{-1} or

$$\Delta H_f = 9086 \pm 100 \text{ cal mol}^{-1} \text{ at } 1162 \text{ K.}$$

According to examinations by Holm[4,5] the eutectic melt should dissolve 1.5–2 mol% Al_2O_3, causing a depression of the freezing point by about 9°. By inserting the correct temperatures and enthalpy of fusion in eqn (2) one obtains

$$\bar{S}_1 = 9090\left(\frac{1}{1153} - \frac{1}{1161}\right) + \frac{\bar{H}_1}{T} \tag{7}$$

or

$$\bar{S}_1 = 0.054 + \frac{\bar{H}_1}{T} \tag{8}$$

The partial enthalpy of mixing Na_3AlF_6 in the system Na_3AlF_6–Al_2O_3 has been determined by Holm[5]. At the composition $N_{Al_2O_3} = 0.01$ (1 mol% Al_2O_3 in the melt), $\bar{H}_{Na_3AlF_6} = 38$ cal mol^{-1}, while $\bar{H}_{Na_3AlF_6} = 102$ cal mol^{-1} at $N_{Al_2O_3} = 0.02$.

By adopting a value for the partial enthalpy in eqn (2) of 70 cal mol^{-1} as the most probable one in the eutectic mixture, one obtains

$$\bar{S}_1 = 0.054 + 0.06\ 1 \tag{9}$$

where the subscript 1 refers to the eutectic mixture. Here the first term corresponds to the assumed "entropy" contribution to the freezing point depression, *i.e.* the value one obtains by setting $\bar{H}_1 = 0$. As shown by eqn (9), however, the contribution from the enthalpy of mixing is even larger than the "entropy" contribution.

This clearly demonstrates that evaluation of "entropy models" from Gibbs free energy data by simply disregarding the enthalpy term can, and often will, lead to directly misleading results even in diluted mixtures.

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