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THE ENTHALPY OF MIXING OF LIQUID NaF AND $NaMgF_3$ FROM DROP CALORIMETRY

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ABSTRACT

The enthalpy of mixing of three liquid mixtures of NaF and $NaMgF_3$ has been measured by drop calorimetry and was found to be negative. This energy release is attributed to a change in the equilibrium

$$Mg_{1/4}[MgF_4^{2-}]_{3/4} + F^- \rightarrow MgF_4^{2-}$$

to the formation of complex MgF_4^{2-}-ions. A ΔH^M diagram for the system NaF–MgF_2 up to 50 mol % MgF_2 has been constructed.

INTRODUCTION

The melting mechanism of the mineral neighbourite, $NaMgF_3$, with the perovskite structure, has been discussed by Holm et al.[1]. They suggested that the heterogenous coordination reaction occurring at the melting point, could be expressed as follows:

$$NaMgF_3(s) \rightleftarrows [Na^+, Mg_{1/4}^{2+}][MgF_4^{2-}]_{3/4}(l) \quad (1)$$

It was assumed that the sodium and the magnesium ions between the first couple of brackets are randomly distributed over positions in an outer shell of the complexed MgF_4^{2-}-ions in the inner shell.

According to the model, additions of NaF to molten $NaMgF_3$ should shift the equilibrium

$$Mg^{2+} (\text{in } MgF_3^-) + F^- \rightarrow MgF_4^{2-} \quad (2)$$

to the right, with corresponding release of energy.

The enthalpy of reaction (2) has now been measured by drop calorimetry using the same technique as reported earlier for other fluoride and chloride mixtures[2–4].

EXPERIMENTAL

Chemicals

Sodium fluoride, NaF, analytical reagent grade (Merck, Germany), was melted before use and clear crystals were selected. Magnesium fluoride, MgF_2, "For the Surface Treatment of Lenses," British Drug Houses, England, was dried in a vacuum furnace at 400 °C before use. Sodium magnesium fluoride, $NaMgF_3$, was prepared by fusing stoichiometric amounts of sodium fluoride and magnesium fluoride in a Pt-crucible in a purified nitrogen atmosphere. The material was checked by X-ray investigation.

Drop calorimetry

The sample was put into a weighed platinum capsule. The air was removed completely by evacuating the capsule which then was filled with purified argon. A lid was then welded on the capsule, and the filled capsule was weighed. The weight of the sample was taken as the difference between that of the filled and the empty capsule. All handling of the sample was done inside a dry-box filled with purified nitrogen.

The enthalpy of fusion was measured by drop calorimetry. The sample was equilibrated in a vertical laboratory furnace and lifted into the calorimeter, which was placed above the furnace.

The calorimeter proper was a silver calorimeter with adiabatic shields. The furnace temperature was measured by a Pt/Pt 10% Rh thermocouple and the calorimeter temperature by a quartz thermometer. The calorimetric set-up has been described in detail elsewhere[5].

RESULTS

The enthalpy of mixing of $NaMgF_3 + NaF$

The results from the drop experiments for Na_2MgF_4 ($N_{MF_2} = 0.33$) are given in Table 1. The results together with the corrected results for the two mixtures

TABLE 1

ENTHALPY INCREMENTS FOR THE MIXTURE $NaF + NaMgF_3$ (Na_2MgF_4)

$T(K)$	$H(T) - H(298.15)$ ($cal_{th}\ mol^{-1}$)		
	Exp.		*Calc.*
	$NaF_{(solid)}$	+	$NaMgF_{3(solid)}$
1001.0	31775		31774
1033.2	33508		33516
1051.5	34545		34535
1084.5	36376		36379
	$Na_2MgF_{4(liquid)}$		
1264.3	68478		68411
1274.2	68886		68964
1285.6	69572		69601
1299.0	70391		70351

0.718 NaF+0.282 $NaMgF_3$ and $NaMgF_3$ published earlier[1], were fitted by a least-squares treatment to equations of the type:

$$H_T - H_{298.15} = a + bT$$

where b corresponds to the assumed constant heat capacity of the solid and the liquid over the limited temperature ranges in question. The results are summarized in Table 2.

TABLE 2

ENTHALPY INCREMENTS $H(T)-H(298.15\ K) = a+bT$ AS A FUNCTION OF TEMPERATURE FOR NaF+MgF_2 MIXTURES

Mixture	*H(T)−H(298.15)* *(cal_{th} mol^{-1})*
0.718 NaF+0.282 $NaMgF_3$ (s)	$-7005+20.04\ T^a$
0.718 NaF+0.282 $NaMgF_3$ (l)	$-4360+25.55\ T^a$
0.5 NaF+0.5 $NaMgF_3$ (s)	$-12007+27.84\ T$
0.5 NaF+0.5 $NaMgF_3$ (l)	$-1132+27.95\ T$
$NaMgF_3$ (s)	$-16404+37.72\ T$
$NaMgF_3$ (l)	$-1059+39.47\ T$

[a] Corrected equation from ref. 1.

The enthalpy of mixing can be calculated from *Cycle 1*. $T = 1300$ K.

Cycle 1

$$\begin{array}{lll} NaF(s) & + NaMgF_3(s) & \\ \downarrow \Delta H_f(NaF) & \downarrow \Delta H_f(NaMgF_3) & \downarrow \Delta H_f(Mix\ 1) \\ NaF(l) & + NaMgF_3(l) \xrightarrow{\Delta H_1} & Na_2MgF_4(l) \end{array}$$

By inserting the enthalpies

ΔH_f (NaF) = 8.1 kcal (Jenssen Holm and Grønvold[6])
ΔH_f ($NaMgF_3$) = 17.7 kcal (Holm et al.[1])
ΔH_f (Mix) = 22.0 kcal (this work)

we obtain

$$\Delta H_1 = \Delta H_f\,(\text{Mix 1}) - \Delta H_f\,(\text{NaF}) - \Delta H_f\,(\text{NaMgF}_3) \quad (4)$$

or

$$\Delta H_1 = 22.0 - 8.1 - 17.7 = -3.8 \text{ kcal mol}^{-1}$$

Hence, for the reaction

$$0.5\ NaF(l) + 0.5\ NaMgF_3(l) = 0.5\ Na_2MgF_4(l)$$

we find $\frac{1}{2}\,\Delta H_1 = -1.9$ kcal mol^{-1}

From the enthalpy of the reaction

$$0.5\ \mathrm{NaF(l)} + 0.5\ \mathrm{MgF(l)} = 0.5\ \mathrm{NaMgF_3(l)}$$

with $\Delta H^{M}_{0.5} = -5.4$ kcal mol^{-1} (Holm et al.[1]) we finally obtain for the mixing process

$$\tfrac{2}{3}\ \mathrm{NaF(l)} + \tfrac{1}{3}\ \mathrm{MgF_2(l)} = \mathrm{Mix}$$

$$\Delta H^{M}_{0.33} = -4.8\ \mathrm{kcal\ mol^{-1}}$$

The enthalpy of mixing of 0.72 NaF+0.28 NaMgF$_3$

The enthalpy of mixing of 0.72 NaF+0.28 NaMgF$_3$ can be calculated from *Cycle 2*. T = 1300 K.

Cycle 2

$$\begin{array}{lll}
0.72\ \mathrm{NaF(s)} & +\ 0.28\ \mathrm{NaMgF_3(s)} & \longrightarrow \\
\downarrow 0.72\ \Delta H_f(\mathrm{NaF}) & \downarrow 0.28\ \Delta H_f(\mathrm{NaMgF_3}) & \downarrow \Delta H_f\ (\mathrm{Mix\ 2}) \\
0.72\ \mathrm{NaF(l)} & +\ 0.28\ \mathrm{NaMgF_3(l)} \xrightarrow{\Delta H_2} & \mathrm{Mix(l)}
\end{array}$$

The cycle results in

$$\Delta H_2 = \Delta H_f\ (\mathrm{Mix\ 2}) - 0.72\ \Delta H_f\ (\mathrm{NaF}) - 0.28\ \Delta H_f\ (\mathrm{NaMgF_3}) \quad (5)$$

By inserting ΔH_f (Mix 2) = 9.7 kcal mol^{-1} (this work) we obtain

$$\Delta H_2 = 9.7 - 5.8 - 4.9 = -1.0\ \mathrm{kcal\ mol^{-1}}$$

Again, for the enthalpy of the process

$$0.28\ \mathrm{NaF(l)} + 0.28\ \mathrm{MgF_2(l)} = 0.28\ \mathrm{NaMgF_3(l)}$$

we get $\Delta H = 0.28 \cdot 2\ \Delta H^{M}_{0.5} = -3.0$ kcal mol^{-1}

For the reaction

$$0.78\ \mathrm{NaF(l)} + 0.22\ \mathrm{MgF_2(l)} = \mathrm{Mix}$$

we obtain $\Delta H^{M}_{0.22} = \dfrac{\Delta H + \Delta H_2}{1.28} = -3.1$ kcal mol^{-1}

as 0.72 mol NaF+0.28 mol NaMgF$_3$ is equivalent to 1.28 mol of the mixture (0.78 NaF+0.22 MgF$_2$).

The three calculated enthalpies of mixing $\Delta H^{M}_{0.22}$, $\Delta H^{M}_{0.33}$ and $\Delta H^{M}_{0.5}$ are plotted in Fig. 1 together with the so-called interaction parameter $\Delta H^{M}/N_{\mathrm{NaF}} \cdot N_{\mathrm{MgF_2}}$, the enthalpy of mixing divided by the product of the two mol fractions.

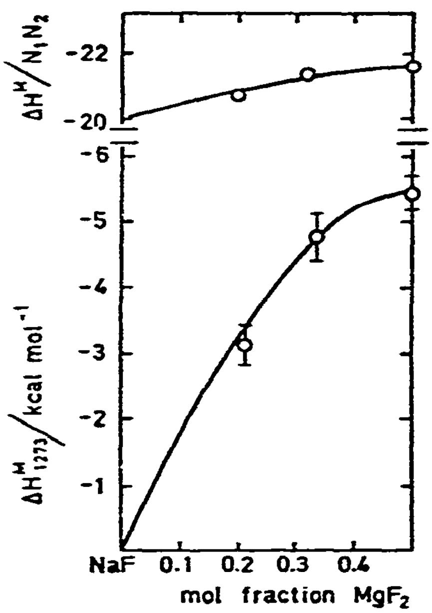

Fig. 1. Calculated enthalpies of mixing of molten NaF and MgF_2 and the interaction parameter $\Delta H^m/N_{NaF} \cdot N_{MgF_2}$.

CONCLUSION

When NaF is added to molten $NaMgF_3$, the enthalpies of mixing are found to be negative. We attribute this energy release to formation of complex MgF_4^{2-}-ions. The simplest way of expressing this is a shift in the coordination equation

$$\underset{\text{outer shell}}{Mg_{1/4}}\underset{\text{inner shell}}{[MgF_4^{2-}]_{3/4}} + F^- \rightarrow \underset{\text{inner shell}}{[MgF_4^{2-}]}$$

where the magnesium ions in the outer shell on the left-hand side will gradually be transferred to the inner and energetically more favorable shell, as shown on the right-hand side of the equation.

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