

Thermodynamic Equilibrium between Melt and Crystalline Phase of a Compound A_qB_r with Dystectic Melting Point

IV. Application to the Systems NaF—NaMgF_3 and KF—KMgF_3

I. PROKS and V. DANĚK

Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava

Received 5 September 2000

The LeChatelier—Shreder equation describing the equilibrium between crystalline phase and melt in the system $A\text{—}AB$ when substance AB partially dissociates upon melting was applied in the systems NaF—NaMgF_3 and KF—KMgF_3 . The dissociation enthalpy, the heat of fusion at dystectic temperature of fusion, and the degree of dissociation of compounds NaMgF_3 and KMgF_3 , formed in the melt, were calculated without using any fictive quantity. The dissociation degrees of NaMgF_3 and KMgF_3 have been found to be $\alpha_+(\text{NaMgF}_3) = 0.23$ and $\alpha_+(\text{KMgF}_3) = 0.11$, respectively.

In the previous paper [1] the LeChatelier—Shreder equation describing the equilibrium between crystalline phase and melt in the system $A\text{—}A_qB_r$ when the substance A_qB_r partially dissociates upon melting was derived without assuming any hypothetical equilibrium states and without the occurrence of any hypothetical thermodynamic quantities. To fit both the phase and the chemical equilibrium in the system $A\text{—}A_qB_r$ an original method for the calculation of the dissociation enthalpy, the heat of fusion at dystectic temperature of fusion, and the degree of dissociation of the compound A_qB_r in the melt was proposed. However, there are not three components in the system, but according to the Gibbs phase law only two. The weighted-in substances A and A_qB_r are thus components and the present substances at equilibrium, A , B , A_qB_r , are called constituents. In order to distinguish between them the components will be in the subsequent text denoted as bold characters, the constituents of the quasi-ternary system as plain ones.

In the present paper the proposed method was applied to the systems NaF—NaMgF_3 and KF—KMgF_3 , which are subsystems of the binary systems NaF—MgF_3 and KF—MgF_2 , in which the additive compounds NaMgF_3 and KMgF_3 , respectively, are formed. In this particular case $q = r = 1$.

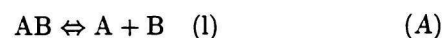
The phase diagram of the system NaF—MgF_3 was measured by *Bergman* and *Dergunov* [2]. These authors found out that a new congruently melting compound NaMgF_3 with the melting point of 1030°C is formed in this system. The coordinates of the individual eutectic points are: 23.2 mole % MgF_3 , 830°C and 62 mole % MgF_2 , 1000°C .

The phase diagram of the system KF—MgF_3 was measured by *DeVries* and *Roy* [3]. Two new com-

pounds are formed in this system. The compound KMgF_3 melts congruently at the temperature of 1070°C , while the compound K_2MgF_4 melts incongruently, with the temperature of peritectic decomposition 846°C . The authors observed a relatively wide range of solid solutions of KF in KMgF_3 with the possible transformation of α to β solid solution near the melting point of KMgF_3 .

The enthalpies of fusion of both intermediate congruently melting compounds NaMgF_3 and KMgF_3 were measured by *Adamkovičová et al.* [4].

The thermodynamic analysis of the systems MF—MMgF_3 ($M = \text{Na, K}$), in which the component MMgF_3 thermally dissociates at melting according to the reaction



is based on the fundamental relations derived in our previous papers [5, 6].

$$\psi = \frac{T T_{\text{fus}}(AB)}{T - T_{\text{fus}}(AB)} \ln \frac{x(AB, T)}{x_+(AB, T)} \quad (1)$$

For limiting values of ψ and its derivative the following relations are valid

$$\lim_{\substack{x_w \rightarrow 1 \\ T \rightarrow T_{\text{fus}}}} \psi = \frac{\Delta_{\text{fus,exp}} H(AB, T_{\text{fus}})}{R} \quad (2)$$

$$\lim_{\substack{x_w \rightarrow 1 \\ T \rightarrow T_{\text{fus}}}} \frac{d\psi}{dx_w} = 0 \quad (3)$$

For the equilibrium mole fractions of individual constituents the following relations, obtained by

means of the weighted-in equilibrium mole fraction, x_w , and the dissociation degree of reaction (A), are valid

$$x(\text{AB}) = \frac{(1 - \alpha_{(A)}(T))x_w}{x_w\alpha_{(A)}(T) + 1} \quad (4)$$

$$x(\text{A}) = \frac{1 - (1 - \alpha_{(A)}(T))x_w}{x_w\alpha_{(A)}(T) + 1} \quad (5)$$

$$x(\text{B}) = \frac{x_w\alpha_{(A)}(T)}{x_w\alpha_{(A)}(T) + 1} \quad (6)$$

For the equilibrium constant of reaction (A) we then get

$$K_{(A),x} = \frac{x(\text{A})x(\text{B})}{x(\text{AB})} = \frac{x_+(A)x_+(B)}{x_+(\text{AB})} = K_{(A),x,+} \quad (7)$$

For ideal solutions eqn (7) holds exactly, for real solutions its validity is assumed for limiting compositions ($x_w \rightarrow 1$, $T \rightarrow T_{\text{fus}}(\text{AB})$).

In the system **KF—KMgF₃** solid solutions of **KF** in the dystectically melting component **KMgF₃** are formed [3]. From the course of the solidus curve it follows, however, that in the solid solution no dissociation of **KMgF₃** takes place. This must be taken into account also in the calculation.

The equilibrium between the liquid and solid solutions is described by the equation

$$\mu(\text{AB}, \text{ss}, x_{w,s}, T) = \mu(\text{AB}, \text{ls}, x_{w,l}, T) \quad (8)$$

where $x_{w,s}$ and $x_{w,l}$ are the equilibrium mole fractions of **AB** in the coexisting solid and liquid solution, respectively.

Assuming the ideal behaviour of the solid solution and inserting for $\mu(\text{AB})_i$ into eqn (8), we get the relation

$$\begin{aligned} \mu_+(\text{AB}, s, T) + RT \ln x_{w,s}(\text{AB}, \text{ss}, T) &= \\ = \mu_+(\text{AB}, l, T) + RT \ln \frac{a(\text{AB}, \text{ls}, x_{w,l}, T)}{a_+(\text{AB}, \text{ls}, T)} \end{aligned} \quad (9)$$

Using eqn (9), relations (1—3) transform to the form [5, 6]

$$\psi_{\text{ss}} = \frac{TT_{\text{fus}}(\text{AB})}{T - T_{\text{fus}}(\text{AB})} \ln \frac{x(\text{AB}, \text{ls}, x_{w,l}, T)}{x_+(\text{AB}, \text{ls}, T) x_{w,s}(\text{AB}, \text{ss}, T)} \quad (10)$$

$$\lim_{\substack{x_{w,l} \rightarrow 1 \\ x_{w,s} \rightarrow 1 \\ T \rightarrow T_{\text{fus}}}} \psi_{\text{ss}} = \frac{\Delta_{\text{fus,exp}}H(\text{AB}, T_{\text{fus}})}{R} \quad (11)$$

$$\lim_{\substack{x_{w,l} \rightarrow 1 \\ x_{w,s} \rightarrow 1 \\ T \rightarrow T_{\text{fus}}}} \frac{d\psi_{\text{ss}}}{dx_{w,l}} = 0 \quad (12)$$

RESULTS AND DISCUSSION

The goal of the calculation in the systems **NaF—NaMgF₃** and **KF—KMgF₃** was to find the values of $\alpha_{(A),+,i}(T_{\text{fus},i})$ to which correspond the limiting values of Ψ and Ψ_{ss} fulfilling eqns (2) and (11) for the calorimetrically measured enthalpies of fusion of **NaMgF₃** and **KMgF₃** [4]. With regard to the limiting conditions, the temperature dependence of $\alpha_{(A),+,i}$ was neglected in the calculation of Ψ and Ψ_{ss} . The functions Ψ and Ψ_{ss} were determined for three equilibrium values of $T_{i,j}$ on the corresponding liquidus, resp. solidus curves taken from [2, 3]. The liquidus curve of **NaMgF₃** in the system **NaF—NaMgF₃** is shown in Fig. 1 and that of **KMgF₃** in the system **KF—KMgF₃** in Fig. 2.

The functions Ψ and Ψ_{ss} were extrapolated for $T_{i,j} \rightarrow T_{\text{fus},i}$ using the regression dependences of the form

$$\Psi_{i,j} = A_{i,j} + B_{i,j}(1 - x_{w,l})^{C_{i,j}} \quad (13)$$

fulfilling the conditions (2) and (11), where

$$A_{i,j} = \frac{\Delta_{\text{fus}}H_{i,j}}{R} \quad (14)$$

For the chosen values of $\alpha_{(A),+,i,j}(T_{\text{fus},i})$ the corresponding values of $\Delta_{\text{fus}}H_{i,j}$ were calculated from the limiting relations (2) and (11). From the empirical relation

$$\varphi_i(\Delta_{\text{fus}}H_{i,j}, \alpha_{(A),+,i}) = 0 \quad (15)$$

the dissociation degrees $\alpha_{(A),+,i}$ were calculated for the calorimetrically measured value of $\Delta_{\text{fus,exp}}H_i$. The results of calculation are summarized in Table 1.

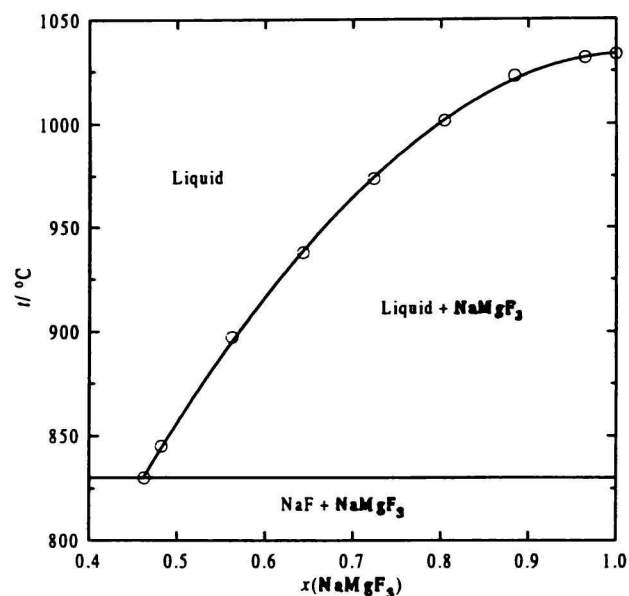


Fig. 1. Liquidus curve of **NaMgF₃** in the system **NaF—NaMgF₃**.

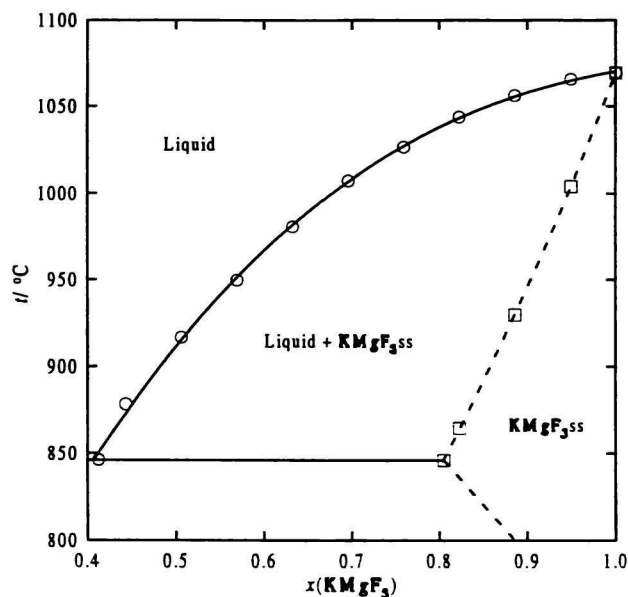


Fig. 2. Liquidus curve of KMgF_3 in the system $\text{KF}-\text{KMgF}_3$.

Table 1. Experimentally Determined Values of the Enthalpies of Fusion and the Calculated Values of the Dissociation Degrees of the Compounds NaMgF_3 and KMgF_3

Component	$\frac{\Delta_{\text{fus,exp}}H(\text{AB}, T_{\text{fus}})}{\text{J mol}^{-1}}$ [5]	$\alpha_{(A),+,i}(T_{\text{fus},i})$
NaMgF_3	$66\,000 \pm 4\,000$	0.23 ₃
KMgF_3	$96\,000 \pm 5\,000$	0.11 ₂

Acknowledgements. The present work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences VEGA under the No. 2/7205/2000.

SYMBOLS

- A, B, AB** components of the binary systems
A, B, AB constituents, *i.e.* the “components” of the quasi-ternary system
 x_w weighted-in mole fraction of **AB** in the system **A—AB**
 $x(\text{AB}, T)$ equilibrium mole fraction of **AB** in the mixture at temperature T
 $T_{\text{fus}}(\text{AB})$ temperature of fusion of **AB**
 $\Delta_{\text{fus,exp}}H(\text{AB}, T_{\text{fus}})$ experimentally determined enthalpy of fusion of **AB** at its temperature of fusion
 $\Delta_{\text{fus}}H_i$ calculated enthalpy of fusion of **AB**
 $\alpha_{(A)}(T)$ dissociation degree of **AB** in reaction (A) at temperature T
 $K_{(A),x}(T)$ equilibrium constant of reaction (A) related to mole fractions in the mixture at temperature T
 $\mu(\text{AB})$ chemical potential of **AB**
 $a(\text{AB})$ activity of **AB** in the mixture
 $A_{i,j}, B_{i,j}, C_{i,j}$ constants in empirical equation
 l liquid
 ls liquid solution
 s solid
 ss solid solution
 + related to pure **AB**

REFERENCES

- Proks, I., Daněk, V., Kosa, L., Nerád, I., and Adamkovičová, K., *Chem. Pap.* 54, 61 (2000).
- Bergman, A. G. and Dergunov, E. P., *Compt. Rend. Acad. Sci. U.S.S.R.* 31, 755 (1941).
- DeVries, R. C. and Roy, R., *J. Am. Chem. Soc.* 75, 2479 (1953).
- Adamkovičová, K., Fellner, P., Kosa, L., Nerád, I., Proks, I., and Strečko, J., *Thermochim. Acta* 242, 24 (1994).
- Proks, I., Daněk, V., Kosa, L., and Adamkovičová, K., *Chem. Pap.*, in press.
- Proks, I. and Daněk, V., *Chem. Pap.*, submitted for publication.