

# Calculation of liquidus curves in phase diagrams

## $\text{Na}_4\text{P}_2\text{O}_7\text{—Mg}_2\text{P}_2\text{O}_7$ and $\text{Na}_4\text{P}_2\text{O}_7\text{—Zn}_2\text{P}_2\text{O}_7$

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Liquidus curves were calculated in the phase diagrams  $\text{Na}_4\text{P}_2\text{O}_7\text{—Mg}_2\text{P}_2\text{O}_7$  and  $\text{Na}_4\text{P}_2\text{O}_7\text{—Zn}_2\text{P}_2\text{O}_7$ . From the phase diagrams and using the method of thermodynamic analogy, the enthalpy of fusion of  $\text{Zn}_2\text{P}_2\text{O}_7$  was determined ( $\Delta H^f = 17 \text{ kcal mol}^{-1}$ ). Good agreement between calculated and experimental data was achieved assuming a partial dissociation of the congruently melting compounds  $\text{Na}_7\text{Mg}_{4.5}(\text{P}_2\text{O}_7)_4$  and  $\text{Na}_2\text{ZnP}_2\text{O}_7$  ( $\alpha^0 = 0.05$ ).

The phase diagrams  $\text{Na}_4\text{P}_2\text{O}_7\text{—Mg}_2\text{P}_2\text{O}_7$  and  $\text{Na}_4\text{P}_2\text{O}_7\text{—Zn}_2\text{P}_2\text{O}_7$  were studied by means of hot-stage microscopy and DTA [1, 2]. The crystallographic description of the present ternary compounds can be found in cited papers. This work deals with theoretical calculations of liquidus curves in the given systems. Because there have been published many papers dealing with the calculation of phase diagrams (*e.g.* [3–5]) we shall present here only equations used in this paper without deriving them in detail.

### Theoretical

In a simple eutectic system it holds

$$d \ln a = \frac{\Delta H_T^f dT}{RT^2} \quad (1)$$

where  $\Delta H_T^f$  is the molar enthalpy of fusion,

$T$  is the temperature of primary crystallization,

$a$  is the activity of the component in the melt,

$R$  is the gas constant.

Assuming that the difference between heat capacity in liquid and solid states of the considered substances is constant ( $\Delta c_p = \text{const}$ ) we obtain by integration of equation (1) the relation

$$\ln a = \frac{\Delta H^f}{R} \left( \frac{1}{T^f} - \frac{1}{T} \right) + \frac{\Delta c_p}{R} \left( \frac{T^f}{T} - 1 - \ln \frac{T^f}{T} \right), \quad (2)$$

where  $T^f$  is the temperature of fusion of a pure component,

$\Delta H^f$  is the enthalpy of fusion of a pure component.

If a chemical compound appears in the binary phase diagram, there is a maximum in the diagram and the shape of the maximum on liquidus curve depends on the degree of dissociation of the compound. Assuming that substance AB dissociates according to the scheme



with the degree of dissociation  $\alpha^0$  and assuming further that the enthalpy of dissociation equals zero, the equilibrium constant  $K$  of equation (3) does not depend on the temperature and can be expressed as

$$K = \frac{\alpha(N_A + \alpha N_{AB})}{(1 - \alpha)(1 + \alpha N_{AB})}, \quad (4)$$

where  $K$  is the constant of dissociation,  
 $\alpha$  is the degree of dissociation of compound AB in mixture AB-A,  
 $N_A, N_{AB}$  are the mole fractions of components in mixture AB-A weighed-in a crucible.

If  $N_{AB} = 1$ , and therefore  $N_A = 0$ ,  $\alpha = \alpha^0$ .

The real mole fraction of component AB in mixture AB-A is

$$x_{AB} = \frac{N_{AB}(1 - \alpha)}{(1 + \alpha N_{AB})}. \quad (5)$$

Assuming that  $\Delta c_p$  of component AB equals zero, we obtain equation similar to equation (2)

$$\ln x_{AB} = \frac{\Delta H^f}{R} \left( \frac{1}{T_0^f} - \frac{1}{T} \right), \quad (6)$$

where  $x_{AB}$  is the real mole fraction of component AB in mixture AB-A,

$T_0^f$  is the hypothetical temperature of fusion of undissociated compound AB.

A more detailed description of the considered method of calculation is in [6].

In the calculation of liquidus curves, it is necessary to express the dependence of the activity of a component in the melt on the composition in a convenient way. It is assumed that the dependence of the activity on the composition can be expressed as

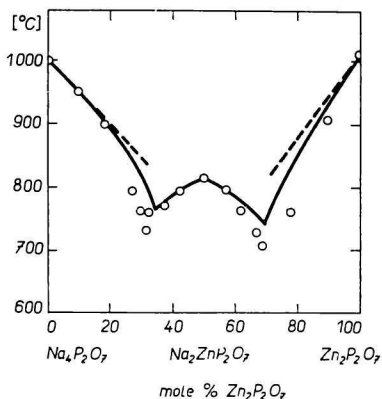


Fig. 1. The phase diagram of the system  $\text{Na}_4\text{P}_2\text{O}_7$ — $\text{Zn}_2\text{P}_2\text{O}_7$ .

— calculation of the activity after equation (7);  
 — calculation of the activity after Temkin's model;  
 ○ experimental data.

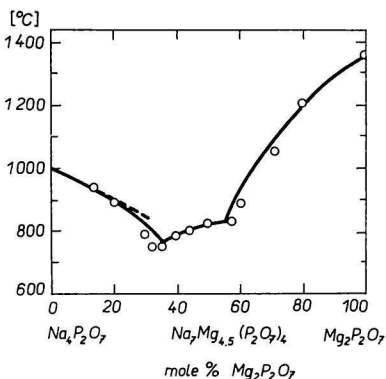


Fig. 2. The phase diagram of the system  $\text{Na}_4\text{P}_2\text{O}_7$ — $\text{Mg}_2\text{P}_2\text{O}_7$ .

— calculation of the activity after equation (7);  
 — calculation of the activity after Temkin's model;  
 ○ experimental data.

$$a = x^k \quad (7)$$

where  $a$  is the activity,

$x$  is the mole fraction,

$k$  is the integer which equals the number of new (foreign) particles brought into the melt.

The liquidus curves calculated on the basis of this assumption are drawn in Figs. 1 and 2 (full line). The dashed lines illustrate the liquidus curve calculated on the basis of Temkin's model [7]. Marking the mole fraction of the first component as  $x$ , the activity of the first component in the systems  $\text{Na}_4\text{P}_2\text{O}_7 - \text{Na}_2\text{ZnP}_2\text{O}_7$  and  $\text{Na}_4\text{P}_2\text{O}_7 - \text{Na}_2\text{MgP}_2\text{O}_7$  can be expressed as

$$a_{\text{Na}_4\text{P}_2\text{O}_7} = \left( \frac{2x + 2}{x + 3} \right)^4 \quad (8)$$

In the systems  $\text{Zn}_2\text{P}_2\text{O}_7 - \text{Na}_2\text{ZnP}_2\text{O}_7$  and  $\text{Mg}_2\text{P}_2\text{O}_7 - \text{Na}_2\text{MgP}_2\text{O}_7$  the activity can be expressed by the relation

$$a_{\text{Zn}_2\text{P}_2\text{O}_7} = \left( \frac{x + 1}{3 - x} \right)^2 \quad (9)$$

### Results and discussion

The results of the calculation of liquidus curves are shown in Figs. 1 and 2. As stated before, the phase diagrams were for calculation formally divided into two parts. After recalculation of the co-ordinates, the results were summarized in one figure. The calculation in both systems  $\text{Na}_4\text{P}_2\text{O}_7 - \text{Zn}_2\text{P}_2\text{O}_7$  and  $\text{Na}_4\text{P}_2\text{O}_7 - \text{Mg}_2\text{P}_2\text{O}_7$  were carried out in a similar way. For a simplicity it was assumed that even in the system  $\text{Na}_4\text{P}_2\text{O}_7 - \text{Mg}_2\text{P}_2\text{O}_7$  the new particles added to the melt were those corresponding to the compound  $\text{Na}_2\text{MgP}_2\text{O}_7$ .

#### *Systems $\text{Na}_4\text{P}_2\text{O}_7 - \text{Na}_2\text{ZnP}_2\text{O}_7$ and $\text{Na}_4\text{P}_2\text{O}_7 - \text{Na}_2\text{MgP}_2\text{O}_7$*

The calculation of liquidus curves was similar in both systems. The component  $\text{Na}_2\text{ZnP}_2\text{O}_7$  and  $\text{Na}_2\text{MgP}_2\text{O}_7$  brings into the melt  $\text{Na}_4\text{P}_2\text{O}_7$  only one new particle ( $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ) and, therefore, the constant  $k$  in equation (7) equals 1. Also Temkin's model (dashed line) describes well the liquidus curve. It is necessary to take into account that good agree-

Table 1

Temperature and molar enthalpy of fusion of some pyrophosphates

Compound	$\Delta H^f$ [kcal mol <sup>-1</sup> ]	$T^f$ [K]	Ref.
$\text{Na}_4\text{P}_2\text{O}_7$	14.0	1273	[8]
$\text{Mg}_2\text{P}_2\text{O}_7$	32.1	1633	[10]
$\text{Ca}_2\text{P}_2\text{O}_7$	24.1	1626	[9]
$\text{Zn}_2\text{P}_2\text{O}_7$	17	1283	
$\text{Na}_2\text{MgP}_2\text{O}_7$	17	1108	
$\text{Na}_2\text{ZnP}_2\text{O}_7$	14.5	1081	

The values of the temperature of fusion are from this work excepting the value for  $\text{Ca}_2\text{P}_2\text{O}_7$ .

ment between calculated and experimental data in the system  $\text{Na}_4\text{P}_2\text{O}_7$ — $\text{Na}_2\text{ZnP}_2\text{O}_7$  up to 30 mole %  $\text{Na}_2\text{ZnP}_2\text{O}_7$  corresponds to 15 mole %  $\text{Zn}_2\text{P}_2\text{O}_7$  in the system  $\text{Na}_4\text{P}_2\text{O}_7$ — $\text{Zn}_2\text{P}_2\text{O}_7$ . The values of enthalpies of fusion are summarized in Table 1. The enthalpy of fusion of  $\text{Na}_2\text{ZnP}_2\text{O}_7$  and  $\text{Na}_2\text{MgP}_2\text{O}_7$  was estimated on the assumption that the entropy of fusion of these components could be evaluated as the sum of entropies of fusion of  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Zn}_2\text{P}_2\text{O}_7$ , and  $\text{Mg}_2\text{P}_2\text{O}_7$  and the ideal entropy of mixing of these components. The part of the phase diagram on the side of the congruently melting compounds  $\text{Na}_2\text{ZnP}_2\text{O}_7$  and  $\text{Na}_2\text{MgP}_2\text{O}_7$  was calculated assuming the degree of dissociation of the compounds  $\alpha^0 = 0.05$ . (The value of  $\alpha^0$  was estimated by a trial and error method.) The calculated curves are in Figs. 1 and 2 (full line). In the system containing  $\text{Na}_7\text{Mg}_{4.5}(\text{P}_2\text{O}_7)_4$ , a correction for the real composition of the congruently melting compound was done.

#### *Systems $\text{Zn}_2\text{P}_2\text{O}_7$ — $\text{Na}_2\text{ZnP}_2\text{O}_7$ and $\text{Mg}_2\text{P}_2\text{O}_7$ — $\text{Na}_2\text{MgP}_2\text{O}_7$*

It is clear that in these cases the congruently melting compound brings into the melt two new particles ( $2\text{Na}^+$ ) and therefore  $k = 2$ . Temkin's model fits the experimental data only in a small concentration range. Better agreement was achieved when the values of the enthalpy of fusion were lower by 2 kcal than those in Table 1. This assumption may be justified by the fact that in the calorimetric value of the enthalpy of fusion the enthalpy of a partial dissociation of the anion  $\text{P}_2\text{O}_7^{4-}$  is included as well. In the calculation of liquidus curves the enthalpy of fusion should correspond to the solidus/liquidus transition without contribution of dissociation. However, the liquidus curves presented in Figs. 1 and 2 are calculated on the basis of literature data. The enthalpy of fusion of  $\text{Zn}_2\text{P}_2\text{O}_7$  was estimated assuming that the entropy of fusion of this compound is equal to the entropy of fusion of  $\text{Ca}_2\text{P}_2\text{O}_7$ . Besides, the enthalpy of fusion determined in this way is in good agreement with the data obtained from the phase diagram.

Comparison of the calculated and the experimental liquidus curves shows that the proposed method of calculation of liquidus curves is suitable for the systems of this type and yields valuable information on the investigated systems.

*The calculations were carried out using a computer CDC 3300 (Calculating Research Centre United Nations D. P., Bratislava).*

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