Thermodynamics of the enantiotropic phase transitions in condensed systems. II. Binary systems*

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The course of the liquidus curve of the component B in a simple eutectic binary system A—B, in which B exists in two modifications, was thermodynamically analyzed. The analysis was performed for the case that T^{tr} was situated between the melting temperature of the component and the eutectic temperature in this system. Two ways were presented to find out the experimentally undeterminable hypothetical melting temperature, T_α^f, and the enthalpy of phase transition ΔH_α^f at T_α^f of the low-temperature modification of component B for the case that the thermodynamic parameters of this component were known. Further it was found that based on the liquidus course the said unknown parameters of the component B could be determined even for the case that ΔH_β^f and ΔH^{tr} were not known. The study of the liquidus diagram of the binary system A—B enabled us to obtain so far unknown information on the component B concerning its polymorphic transformation.

Let us consider a simple eutectic system A—B. The component B exists in it in two polymorphous modifications, *i.e.* the low-temperature (α) and the high-temperature (β) modification. With respect to the equilibrium "solidus—liquidus" such a case is interesting, for which the relation $T_E < T^{tr} < T_\beta^f$ holds (T_E being the eutectic temperature in the system A—B, T^{tr} the temperature of the transition $B_\alpha \rightleftarrows B_\beta$, and T_β^f the melting temperature of the high-temperature modification B_β).

An isobaric phase diagram of the considered type is shown in Fig. 1. There are two invariant points in this diagram, *viz.* the point E and the point Q. The point Q corresponds to the equilibrium $L_Q \rightleftarrows B_\alpha^s + B_\beta^s$ (L_Q is the liquid phase in the composition given. by the point Q, $B_{\alpha(\beta)}^s$ is the solid phase of the α- and β-modification of the component B)

The liquidus curve of the component B exhibits a break representing the intersection point of the curves $T_\beta^f Q$ and $T_\alpha^f E$. Under the equilibrium conditions the liquidus curves $\widehat{T_\beta^f Q}$ and $\widehat{Q E}$ are experimentally measurable. The hypothetical melting temperature of the low-temperature modification, T_α^f, and the corresponding enthalpy change of ΔH_α^f at T_α^f cannot be determined in the equilibrium state. It is however inevitable to know them for the theoretical calculation of the liquidus course of the component B on the part $\widehat{Q E}$ of the curve.
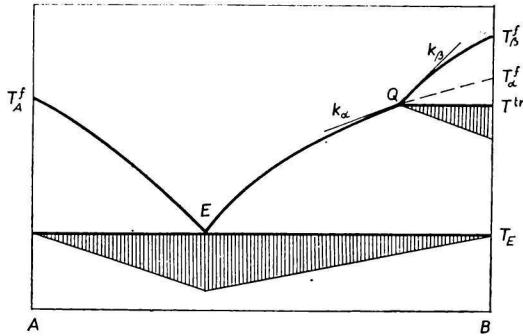

Fig. 1. Phase diagram of the simple eutectic binary system A — B, in which the component B exists in two modifications.
Hatching shows the Tamman triangles.

The paper [1] presents the calculation of these quantities in one-component systems. In the present paper the problem of determining these values is being solved for simple eutectic binary systems.

1. *Thermodynamic parameters T_β^f, ΔH_β^f, T^{tr}, ΔH^{tr}, C_P^l, C_P^β, C_P^α are known.*

1.1. Let us suppose that ΔC_P of the phase transitions "solidus—liquidus" are zero.

Then for the point Q at the temperature T^{tr} the equation holds

$$\ln a_\beta = \Delta H_\beta^f \cdot R^{-1} \left[\frac{1}{T_\beta^f} - \frac{1}{T^{tr}} \right], \tag{1}$$

where a_β is the activity of the component B in the liquid phase in the point Q, being in equilibrium with the solid β-modification of the component B.

For the point Q at the same temperature eqn (2) is valid:

$$\ln a_\alpha = \Delta H_\alpha^f \cdot R^{-1} \left[\frac{1}{T_\alpha^f} - \frac{1}{T^{tr}} \right], \tag{2}$$

where analogously, a_α is the activity of the component B in the liquid phase in the point Q, being in equilibrium with the solid α-modification of the component B.

For $\Delta C_P^{l/s} = 0$ it holds

$$\Delta H_\alpha^f = \Delta H_\beta^f + \Delta H^{tr}. \tag{3}$$

In the point Q the liquid phase is in equilibrium with two solid phases that are also mutually in equilibrium.

For the temperature T^{tr} the relation holds $a_\alpha = a_\beta$; by introducing eqn (3) into eqn (2) and simultaneous solution of eqns (1) and (2) we obtain the hypothetical melting temperature of the low-temperature modification of B.

$$T_\alpha^f = \frac{(\Delta H_\beta^f + \Delta H^{tr}) \, T^{tr} \cdot T_\beta^f}{\Delta H_\beta^f \cdot T^{tr} + \Delta H^{tr} \cdot T_\beta^f} \, . \tag{4}$$

1.2. Let us suppose that ΔC_P of the phase transitions "solidus—liquidus" are not zero.

Then for the activity a_β of the component B in the point Q at the temperature T^{tr} the following equation holds

$$R \cdot T^{tr} \cdot \ln a_\beta = -\Delta H_\beta^f \left[1 - \frac{T^{tr}}{T_\beta^f} \right] + \int_{T^{tr}}^{T_\beta^f} \Delta C_P^{l/\beta} \, dT - T^{tr} \int_{T^{tr}}^{T_\beta^f} \Delta C_P^{l/\beta} \, d\ln T. \tag{5}$$

Since all the quantities on the right-hand side are known, a_β for the temperature T^{tr} can be readily computed.

Analogously for the activity a_α of B_α in the same point Q and at the same temperature T^{tr} it holds

$$R \cdot T^{tr} \cdot \ln a_\alpha = -\Delta H_\alpha^f \left[1 - \frac{T^{tr}}{T_\alpha^f} \right] + \int_{T^{tr}}^{T_\alpha^f} \Delta C_P^{l/\alpha} \, dT - T^{tr} \int_{T^{tr}}^{T_\alpha^f} \Delta C_P^{l/\alpha} \, d\ln T. \tag{6}$$

Since for T^{tr} it holds $a_\alpha = a_\beta$, the activity a_α is known. There are, however, on the right-hand side of eqn (6) two unknown quantities, *viz.* the hypothetical melting temperature T_α^f and the corresponding melting enthalpy ΔH_α^f. Therefore it is necessary to find another independent equation containing only these two quantities as unknown parameters. We will obtain this equation in the following manner.

For the transition temperature T^{tr} it holds

$$\Delta H_{T^{tr}}^{l/\alpha} = \Delta H_{T^{tr}}^{l/\beta} + \Delta H^{tr} \tag{7}$$

then

$$\Delta H_{T^{tr}}^{l/\beta} = \Delta H_\beta^f - \int_{T^{tr}}^{T_\beta^f} \Delta C_P^{l/\beta} \, dT. \tag{8}$$

Likewise it holds

$$\Delta H_{T^{tr}}^{l/\alpha} = \Delta H_\alpha^f - \int_{T^{tr}}^{T_\alpha^f} \Delta C_P^{l/\alpha} \, dT \tag{9}$$

and comparing eqns (7—9) we obtain eqn (10).

$$\Delta H_\alpha^f = \Delta H_\beta^f + \Delta H^{tr} - \int_{T^{tr}}^{T_\beta^f} \Delta C_P^{l/\beta} \, dT + \int_{T^{tr}}^{T_\alpha^f} \Delta C_P^{l/\alpha} \, dT. \tag{10}$$

Then eqns (6) and (10) enable us to determine both T_α^f and ΔH_α^f.

For the computation of these two quantities, T_α^f and ΔH_α^f, also another procedure may be used.

We transform the activity coordinates in the functional dependence $a_B^l = f(T)$ as follows

$$a_{T^{tr}} : a_{T^{tr}}^* = a_{T_\alpha^f} : a_{T_\alpha^f}^* , \tag{11}$$

where $a_{T^{tr}}$, $a_{T_\alpha^f}$ denote the original activity of the component B in the solution, saturated with this component at T^{tr} and T_α^f, respectively; $a_{T^{tr}}^*$, $a_{T_\alpha^f}^*$ are the transformed activities of the same component and at the same temperatures.

Usually one chooses $a_{T_\alpha^f} = 1$, and then $a_{T^{tr}} \neq 1$.

Let us choose $a_{T^{tr}}^{\bullet} = 1$; then from eqn (11) it follows that

$$a_{T_{\alpha}^{f}}^{\bullet} = \frac{a_{T^{tr}}^{\bullet} \cdot a_{T_{\alpha}^{f}}}{a_{T^{tr}}} = \frac{1}{a_{T^{tr}}} \qquad (12)$$

and

$$\ln a_{T_{\alpha}^{f}}^{\bullet} = -\ln a_{T^{tr}} \qquad (13)$$

respectively.

Then for the activity $a_{T_{\alpha}^{f}}^{\bullet}$ we obtain

$$R \cdot T_{\alpha}^{f} \cdot \ln a_{T_{\alpha}^{f}}^{\bullet} = -\Delta H_{T^{tr}}^{l/\alpha} \left[1 - \frac{T_{\alpha}^{f}}{T^{tr}} \right] + \int_{T_{\alpha}^{f}}^{T^{tr}} \Delta C_{P}^{l/\alpha} \, \mathrm{d}T - T_{\alpha}^{f} \int_{T_{\alpha}^{f}}^{T^{tr}} \Delta C_{P}^{l/\alpha} \, \mathrm{d}\ln T. \qquad (14)$$

Since $\Delta H_{T^{tr}}^{l/\alpha}$ can be determined using eqn (7), the only unknown quantity with respect to relation (14) is the temperature T_{α}^{f}.

We will apply the procedure of the transformed activity coordinates to the computation of T_{α}^{f} and ΔH_{α}^{f} for CaF_2 in the system $LiF-CaF_2$ and use for this purpose the data according to *Naylor* [2]:

$T_{\beta}^{f} \quad = 1691 \text{ K}$
$\Delta H_{\beta}^{f} = 7100 \text{ cal mol}^{-1}$
$C_{P}^{l} \quad = 23.88 \text{ gibbs mol}^{-1}$
$C_{P}^{\beta} \quad = (25.81 + 2.5 \times 10^{-3} \, T) \text{ gibbs mol}^{-1}$
$C_{P}^{\alpha} \quad = (14.30 + 7.28 \times 10^{-3} \, T + 4.69 \times 10^{5} \, T^{-2}) \text{ gibbs mol}^{-1}$
$T^{tr} \quad = 1424 \text{ K}$
$\Delta H^{tr} = 1140 \text{ cal mol}^{-1}$

Considering the simplified case that $\Delta C_P = 0$ (eqn (4)), then

$$a_Q = 0.673, \quad \Delta H_{\alpha}^{f} = 8240 \text{ cal mol}^{-1}, \quad T_{\alpha}^{f} = 1648.18 \text{ K}.$$

If we take the values of C_P according to [2] and apply eqn (14), then $a_Q = 0.642$, $a_{\alpha}^{\bullet} = 1.56$ and

$$T_{\alpha}^{f} = 1637 \text{ K}; \quad \Delta H_{\alpha}^{f} = 9428.13 \text{ cal mol}^{-1}.$$

The calculated liquidus curve of CaF_2 (α- and β-modifications) in the system $LiF-CaF_2$ is presented in paper [3].

2. *Only the values T_{β}^{f} and T^{tr} are known, while ΔH_{β}^{f}, ΔH^{tr}, and all C_P values are unknown.*

For this case the above-discussed procedure cannot be applied. Therefore by means of the TA method we shall determine the liquidus of the component B and the point Q with a highest possible accuracy (see Fig. 1).

2.1. Difference between T^{f} and T^{tr} is not too great (up to approx. 100°C).

In this case the point Q is usually situated near the melting point of the pure component B. The activity a_B may be therefore expressed with a satisfactory precision using the universal relationship [4] as

$$a_B = x_B^{k_{A/B}^{St}},$$

where $k_{A/B}^{St}$ denotes the number of particles appearing in the system formed by the pure substance B, as a consequence of 1 molecule of substance A brought in into the system. If $T^f - T^{tr}$ is less than 100°C, then the 3rd and 4th terms on the right-hand side of eqn (5) may be supposed to be negligible and we may use eqn (2).

For the computation of ΔH_β^f and ΔH^{tr} the relation $\ln x_B = f(T_B^{-1})$ can be applied:

$$\ln a_B = k_{A/B}^{St} \cdot \ln x_B = \frac{\Delta H_B^f}{R} \left[\frac{1}{T_B^f} - \frac{1}{T_B} \right],$$

$$\ln x_B = q - k \cdot \frac{1}{T_B}. \tag{15}$$

Since the graphical representation of the dependence $\ln x = f(1/T)$ is a straight line, it is possible to determine the values of ΔH_β^f and ΔH_α^f from the slope of this line. In Fig. 2 the course of the dependence $\ln x = f(1/T)$ is presented for three different values of k^{St}.
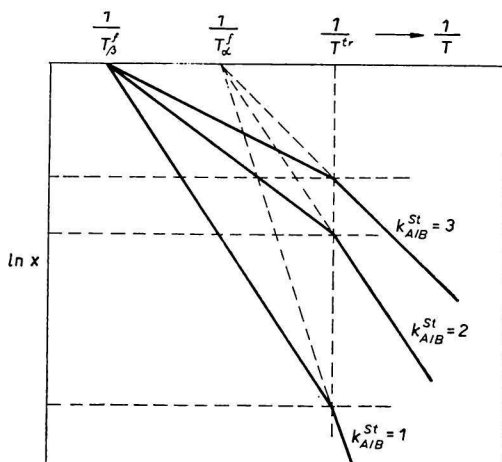

Fig. 2. The course of the dependence $\ln x_B^{k_{A/B}^{St}} = f(T^{-1})$ for $k_{A/B}^{St} = 1, 2, 3$.

The straight lines passing through the points $1/T_\beta^f$ and $1/T_\alpha^f$ can be used to compute the magnitudes of ΔH_β^f and ΔH_α^f, respectively. The difference between ΔH_α^f and ΔH_β^f equals ΔH^{tr}. The value of T_α^f can be obtained either using eqn (4) or graphically from Fig. 2.

2.2. Difference $T_\beta^f - T^{tr} > 100°C$. (An approximate procedure.)

For this case the missing thermodynamic parameters will be determined in the following way. Again it is supposed that the liquidus course of the component B in the system A—B is known and that the point Q has been determined. It should be noted that it is advantageous to choose for the component A such a substance, for which it unambiguously holds that $k_{A/B}^{St}$ is an integer. The liquidus of B is evaluated by cryometry for $x_B \to 1$ and ΔH_β^f calculated. For the point Q the criterion of the thermodynamic consistence III [5] is applied in the simplified form

$$\Delta H_\beta^f \cdot k_\beta = \Delta H_\alpha^f \cdot k_\alpha$$

and ΔH_α^f is obtained. The computation of T_α^f will be carried out using eqn (*4*). ΔH_α^f and ΔH_β^f are known, which makes it possible to determine the magnitude of ΔH^{tr} (eqn (*7*)). By introducing the value of ΔH_β^f into eqn (*1*) the activity of the component B in the point Q at the transition temperature T^{tr} is obtained. The comparison of this value with the experimentally obtained concentration coordinate of the point Q will demonstrate to what extent the accepted simplifications have been justified.

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