Equation of the liquidus curve in simple eutectic systems*

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Several methods of derivation of the generalized LeChatelier—Schröder equation which describes the course of the liquidus curves in binary systems with a simple eutectic have been compared. From this analysis it follows that the activity of the i-th component in its at equilibrium saturated liquid solution is a function of the molar enthalpy of fusion of this pure component, *i.e.*, $\Delta H_i^{0,1/0,s}$ Further, the phenomenon of the retrograde solubility of substances in binary systems of the given type is discussed.

Обсуждается несколько способов получения обобщенного уравнения ЛеШателье—Шредера, описывающего ход кривых ликвидуса в двойных системах с простой эвтектикой. Из анализа вытекает, что активность i-ой компоненты в ее насыщенном жидком растворе является функцией изменения мольной энтальпии этой чистой компоненты при плавлении, т.е. $\Delta H_i^{0,1/0,s}$. Обсуждалось явление ретроградной растворимости веществ в двойных системах.

1. Derivation of the LeChatelier—Schröder equation

In the calculation of the course of liquidus curves in the binary simple eutectic systems the equation which we shall call the *generalized LeChatelier—Schröder equation* is used

$$\ln a_{i,\text{eq}}^{1} = \Delta H_i^{0,1/0,s} [1/T_i^f - 1/T_i]/R. \qquad (1)$$

$a_{i,\text{eq}}^{1}$ is the activity of the i-th component in its liquid saturated solution in equilibrium with the pure substance i,

$\Delta H_i^{0,1/0,s}$ is the change of the molar enthalpy of the substance i in the process "*solidus$\rightarrow$liquidus*" For the sake of simplicity we shall assume it to be constant, *i.e.*, temperature independent (at $P = \text{const}$),

T_i^f is the melting point (K) of pure component i,

T_i is the temperature of the primary crystallization of the pure component i

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in a liquid solution (or melt) which is saturated with this component and where the activity of this component equals $a'_{i,e}$

Different relations have been used in the literature to describe the dependence $a'_{i,eq} = f(T_i)$. Thus, *e.g.*, in the monographs by *Blander* ([1], pp. 140 and 255), *Denbigh* ([2], p. 283), and by *Prigogine* and *Defay* ([3], p. 377) relations principally conformable to eqn (*1*) are presented, whereas in others (*e.g.* in the monograph by *Kogan* [4], p. 101, eqn. *III-50*) the activity $a'_{i,eq}$ is considered to be a function of the quantity $\Delta \bar{H}_i^{l/0,s} = \bar{H}_i^l - H_i^{0,s}$ (where $\bar{H}_i^l$ is the partial molar enthalpy of the component i in a liquid solution saturated with this component), instead of the change of the molar enthalpy of fusion of pure substance i, $\Delta H_i^{0,l/0,s} = H_i^{0,l} - H_i^{0,s}$ This different approach initiated the present study.

1.1. Application of the method of the isothermal-isobaric ΔG cycle

The condition of the thermodynamic equilibrium, *e.g.*, for the component B (Fig. 1, $\bar{B}^l \rightleftharpoons B^{0,s}$), at T, P = const is expressed by the equation

$$\bar{G}_B^l = G_B^{0,s},$$

where $\bar{G}_B^l$ is the partial molar Gibbs energy of the component B in its saturated liquid solution and $G_B^{0,s}$ is the molar Gibbs energy of the pure substance B in the solid state.

Standard states were chosen as follows: a) pure substance B in the form of undercooled liquid, denoted as $B^{0,l}$, b) pure substance B in the solid state, denoted as $B^{0,s}$ It holds obviously that $\Sigma \Delta G_B^{p/q} = 0$ (Fig. 2) and hence (index "B" is omitted)

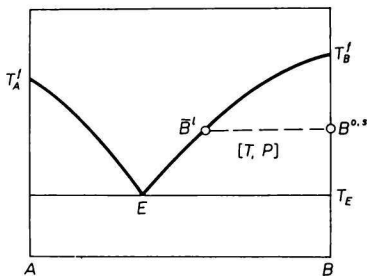$$\Delta G^{2/1} + \Delta G^{1/3} + \Delta G^{3/2} = 0$$

Fig. 1. Isobaric phase diagram of the binary system A—B with a simple eutectic. The equilibrium $\bar{B}^l \rightleftharpoons B^{0,s}$ is shown.
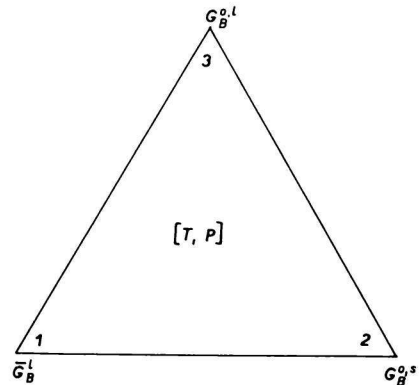
Fig. 2. Isothermal-isobaric ΔG cycle for the phase equilibrium $\bar{B}^l \rightleftharpoons B^{0,s}$ in a binary system with a simple eutectic.

Obviously

$$\Delta G^{2/1} = G^{0,s} - \bar{G}^l = 0 \, ,$$

$$\Delta G^{1/3} = \bar{G}^l - G^{0,l} = RT \ln a_{eq}^l \, ,$$

$$\Delta G^{3/2} = G^{0,l} - G^{0,s} = \Delta G^{0,l/0,s}$$

By substituting these expressions into the relation $\Sigma\Delta G^{p/q}$ we obtain

$$RT \ln a_{eq}^l = -\Delta G^{0,l/0,s} = -[\Delta H^{0,l/0,s} - T\,\Delta S^{0,l/0,s}] \tag{2}$$

If $\Delta C_P^{0,l/0,s} = 0$, then $\Delta H^{0,l/0,s} = \Delta H^f$ (= the enthalpy of fusion of the pure component at its melting point), $\Delta S^{0,l/0,s} = \Delta S^f = \Delta H^f/T^f$ and by rearranging we get eqn (1).

The method of isothermal-isobaric ΔG cycle affords the searched dependence in the form $\ln a_{i,eq}^l = f(T_i)$. We shall denote it as an *"integral"* method.

1.2. Application of the Planck function $-G/T$

The equilibrium of this type is stipulated by a simultaneous validity of eqn (3) and (4) at $P = \text{const}$

$$\bar{G}^l/T = G^{0,s}/T \qquad (equil.) \, , \tag{3}$$

$$d(\bar{G}^l/T) = d(G^{0,s}/T) \qquad (equil.) \tag{4}$$

At $P = \text{const}$, $\bar{G}^l = f(T, x)$, where x is the mole fraction of the substance B in the liquid saturated solution; $G^{0,s} = f(T)$. As $\bar{G}^l = G^{0,l} + RT \ln a^l$, it holds with respect to eqn (4)

$$\frac{\partial}{\partial T}\left[\frac{G^{0,l} + RT \ln a^l}{T}\right]_x \mathrm{d}T_{eq} + \frac{\partial}{\partial x}\left[\frac{G^{0,l} + RT \ln a^l}{T}\right]_T \mathrm{d}x_{eq} = \frac{\partial}{\partial T}\left[\frac{G^{0,s}}{T}\right] \mathrm{d}T_{eq}$$

It holds that $\dfrac{\partial}{\partial x}\left[\dfrac{G^{0,l}}{T}\right]_T = 0$. By rearranging we get

$$R\left[\left(\frac{\partial \ln a^l}{\partial T}\right)_x \mathrm{d}T_{eq} + \left(\frac{\partial \ln a^l}{\partial x}\right)_T \cdot \mathrm{d}x_{eq}\right] = -\frac{\partial}{\partial T}\left[\frac{G^{0,l} - G^{0,s}}{T}\right] \cdot \mathrm{d}T_{eq}$$

As $\dfrac{\partial}{\partial T}\left[\dfrac{G}{T}\right]_{x,P} = \dfrac{-H_{x,P}}{T^2}$,

$$\mathrm{d} \ln a_{eq}^l(T, x) = \frac{\Delta H^{0,l/0,s}}{RT^2} \cdot \mathrm{d}T_{eq} \, , \tag{5}$$

where

$$\Delta H^{0,l/0,s} = H^{0,l} - H^{0,s}$$

Eqn (5) is obviously the differential form of eqn (1). The application of the Planck function affords the searched dependence in the form d ln $a^l_{i,eq} = f(T_i)_{eq}$, hence it may be denoted as a *"differential"* method.

1.3. Application of the relation $a^l = f(T, x)$

For the equilibrium of the given type it formally holds that $a^l = f(T, x)$, $P = \text{const}$, and consequently also $\ln a^l = f_1(T, x)$. Both a^l and $\ln a^l$ are functions of state. Then using the properties of exact differentials (see, *e.g.*, [2], p. 255) we can write

$$\text{d} \ln a^l = (\partial \ln a^l/\partial T)_x \ \text{d}T + (\partial \ln a^l/\partial x)_T \ \text{d}x \qquad (6)$$

Eqn (6) can be integrated if the both right-hand terms are known.

From the derivation of the definition equation $\bar{G}^l = G^{0,l} + RT \ln a^l$ with respect to T at $x = \text{const}$ it follows

$$(\partial \ln a^l/\partial T)_x = (1/R) \ [\partial(\bar{G}^l - G^{0,l}/T)/\partial T]_x$$

or

$$(\partial \ln a^l/\partial T)_x = -\frac{(\bar{H}^l - H^{0,l})_x}{RT^2} \qquad (7)$$

Thus the first right-hand term of eqn (6) has been established.

The second term will be determined by means of eqn (4) applied to the phase equilibrium $\bar{B}^l \rightleftharpoons B^{0,s}$

$$[\partial(\bar{G}^l/T)/\partial T]_x \ \text{d}T_{eq} + [\partial(\bar{G}^l/T)/\partial x]_T \ \text{d}x_{eq} = [\partial(G^{0,s}/T)/\partial T] \ \text{d}T_{eq}$$

or

$$-[(\bar{H}^l)_x/T^2] \ \text{d}T_{eq} + [\partial(G^{0,l} + RT \ln a^l_{eq}/T)/\partial x]_T \ \text{d}x_{eq} = -(H^{0,s}/T^2) \ \text{d}T_{eq}$$

and after some rearrangement

$$(\partial \ln a^l_{eq}/\partial x)_T \ \text{d}x_{eq} = \frac{(\bar{H}^l - H^{0,s})_x}{RT^2} \cdot \text{d}T_{eq} \qquad (8)$$

Eqn (8) is the second right-hand term of eqn (6). By substituting the corresponding terms from eqns (7) and (8) into eqn (6) we get

$$\text{d} \ln a^l_{eq} = \frac{(-\bar{H}^l + H^{0,l})_x}{RT^2} \cdot \text{d}T_{eq} + \frac{(\bar{H}^l - H^{0,s})_x}{RT^2} \cdot \text{d}T_{eq}$$

or

$$\mathrm{d} \ln a^{\mathrm{l}}_{\mathrm{eq}} = \frac{\Delta H^{0,1/0,s}}{RT^2} \cdot \mathrm{d} T_{\mathrm{eq}} \tag{9}$$

since the terms $-\bar{H}^{\mathrm{l}}$ and $+\bar{H}^{\mathrm{l}}$ are cancelled out. Eqn (9) is obviously identical with eqn (5) and it is the differential form of eqn (1).

2. Phenomenon of retrograde solubility in binary systems of the given type

Generally, the solubility of a substance in its saturated solution increases with increasing temperature, *i.e.*, its mole fraction in the liquid phase, $x^{\mathrm{l}}_{i,\mathrm{eq}}$ increases with temperature (up to $T_i = T_i^{\mathrm{f}}$). However, in some particular cases in a determined temperature interval the value of $x^{\mathrm{l}}_{i,\mathrm{eq}}$ decreases with increasing temperature. This phenomenon is usually denoted as retrograde solubility ([5], p. 82; [6], p. 235). It means that the dependence $x^{\mathrm{l}}_{i,\mathrm{eq}} = \mathrm{f}(T_i)$ ceases to be single-valued, *i.e.*, to a given composition of the system two different temperatures can be determined at which the system becomes saturated with the same i-th component. The phenomenon of the retrograde solubility has been observed, *e.g.*, in the systems Li_2SO_4—H_2O ([5], p. 81; [7], p. 1409) and Na_2SO_4—H_2O ([6], p. 236; [7], p. 1639).

The conditions for the appearance of this phenomenon can be determined on the basis of eqn (8) from which it follows

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) = \frac{RT^2 \left(\frac{\partial \ln a^{\mathrm{l}}_{\mathrm{eq}}}{\partial x}\right)_T}{(\bar{H}^{\mathrm{l}} - H^{0,s})_x}. \tag{10}$$

It holds that

$$\bar{H}^{\mathrm{l}} - H^{0,s} = \Delta \bar{H}^{\mathrm{l}/0,s} = (\bar{H}^{\mathrm{l}} - H^{0,1}) + (H^{0,1} - H^{0,s}),$$

$$\bar{H}^{\mathrm{l}} - H^{0,s} = \Delta \bar{H}^{\mathrm{l}}_{\mathrm{mix}} + \Delta H^{0,1/0,s}$$

Hence

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{\mathrm{eq}} = \frac{RT^2 \left(\frac{\partial \ln a^{\mathrm{l}}_{\mathrm{eq}}}{\partial x}\right)_T}{(\Delta \bar{H}^{\mathrm{l}}_{\mathrm{mix}} + \Delta H^{0,1/0,s})_x}. \tag{11}$$

The term $\Delta H^{0,1/0,s}$ is always greater than zero.

Concerning the term $(\partial \ln a^{\mathrm{l}}_{\mathrm{eq}}/\partial x)_T$, the situation is somewhat more complicated.

Let us suppose, that in a given system only one liquid phase exists, as it is the case in systems of simple eutectic type, and that the slope of the tangent to the liquidus curve of each of the two components of this system never equals zero. Then the
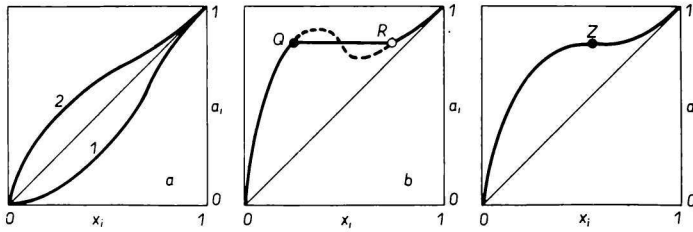
Fig. 3. Principal possibilities of the dependence of activity on composition.
a) Curve 1 — negative deviation from ideality, curve 2 — positive deviation from ideality, for both cases it holds $(\partial \ln a^l_{eq}/\partial x)_T > 0$;
b) $(\partial \ln a^l_{eq.Q}/\partial x)_T > 0$, $(\partial \ln a^l_{eq.R}/\partial x)_T > 0$;
c) $(\partial \ln a^l_{eq.Z}/\partial x)_T = 0$

course of the dependence $a_i = f(x_i)$ is monotonous over the whole concentration range. In this case it holds therefore

$$(\partial \ln a^l_{eq}/\partial x)_T > 0$$

This possibility is presented in Fig. 3a (the curves correspond to positive and negative deviation from ideality, respectively, and the diagonal expresses the validity of Raoult's law, i.e., $a_i = x_i$).

There is another possibility, viz., that in the system under consideration two liquid phases exist in equilibrium. This situation is typical for systems exhibiting a miscibility gap and is associated with a sufficiently great positive deviation from ideality. In this case the course of the function $a_i = f(x_i)$ is not monotonous any more. The two liquids of composition corresponding to the point Q and R are evidently in equilibrium. Single-phase solutions with composition coordinates situated between the points Q and R are metastable with respect to the two-phase system ([8], p. 329).

Nevertheless for the activities of the given component i in the co-existing liquid phases of the compositions corresponding to the points Q and R it holds again

$$(\partial \ln a^l_{eq.Q}/\partial x)_T > 0 , \qquad (\partial \ln a^l_{eq.R}/\partial x)_T > 0$$

as it is graphically demonstrated in Fig. 3b.

However, there is still the third possibility which is schematically presented in Fig. 3c. For all points of the curve $a_i = f(x_i)$ it holds $(\partial \ln a^l_{eq}/\partial x)_T > 0$, but with the exception of the point Z. For this

$$(\partial \ln a^l_{eq.Z}/\partial x)_T = 0$$

The presented relation expresses the condition for imminent immiscibility. This special case is not included in the present considerations.

Nevertheless in this connection should be mentioned that Karapetyants ([9], p. 265) says that for the "solidus—liquidus" equilibrium it holds

$$(\partial \bar{G}_i/\partial x_i)_T > 0$$

But $\bar{G}_i = G_i^0 + RT \ln a_i$, and for the considered phase equilibrium it should be written

$$\bar{G}_{i,\text{eq}}^l = G_i^{0,l} + RT \ln a_{i,\text{eq}}^l$$

and

$$(\partial \bar{G}_{i,\text{eq}}^l/\partial x_i)_T = RT(\partial \ln a_{i,\text{eq}}^l/\partial x_i)_T \gtrless 0$$

Consequently we can conclude that the above-mentioned relation $(\partial \bar{G}_i/\partial x_i)_T > 0$ has not the general validity.

Hence, after returning to our analysis we see that it is necessary to distinguish three possibilities (Fig. 4)

$$\text{I.} \quad \Delta \bar{H}_{\text{mix,B}} + \Delta H_{\text{B}}^{0,l/0,s} > 0$$

Then $(\mathrm{d}T/\mathrm{d}x)_{\text{eq}} > 0$ and this condition corresponds to the part $T'Z$ on the liquidus curve of the component B

$$\text{II.} \quad \Delta \bar{H}_{\text{mix,B}} + \Delta H_{\text{B}}^{0,l/0,s} \doteq 0$$

Then $(\mathrm{d}T/\mathrm{d}x)_{\text{eq}} \to \infty$ and this relation corresponds to the point Z on the liquidus curve of the component B

$$\text{III.} \quad \Delta \bar{H}_{\text{mix,B}} + \Delta H_{\text{B}}^{0,l/0,s} < 0$$

Then $(\mathrm{d}T/\mathrm{d}x)_{\text{eq}} < 0$ and this relation corresponds to the part ZE on the liquidus curve of the component B.

The correctness of the above conclusions can be proved also by means of the criteria of thermodynamic consistency for the course of liquidus curves in binary systems without solid solutions.

For the vicinity of the eutectic point of the systems with a simple eutectic criterion II [10—12] holds

$$x_\text{A} \; \Delta \bar{H}_\text{A}^{l/0,s} \; k_\text{A} = x_\text{B} \; \Delta \bar{H}_\text{B}^{l/0,s} \; k_\text{B} \tag{12}$$

k_A and k_B are the slopes of tangents to the liquidus curves of the components A and B, respectively, in the eutectic point. Consequently, $k_i = (\mathrm{d}T/\mathrm{d}x_i)_{\text{eq,E}}$.

For the system A—B (Fig. 4) it holds obviously, that x_A, $\Delta \bar{H}_\text{A}^{l/0,s}$, k_A, $x_\text{B} > 0$, $k_\text{B} < 0$ (all terms are considered in the eutectic point E). Then according to eqn (12) it must hold that $\Delta \bar{H}_\text{B}^{l/0,s} < 0$. But $\Delta \bar{H}_\text{B}^{l/0,s} = \Delta \bar{H}_{\text{mix,B}} + \Delta H_\text{B}^{0,l/0,s}$. If the left side in this equation is less than zero so must be the right side, too, and this is just the above-mentioned case III.

For the vicinity of the peritectic point P in a system without solid solubility with an incongruently melting compound M (Fig. 5) criterion IV [12] holds
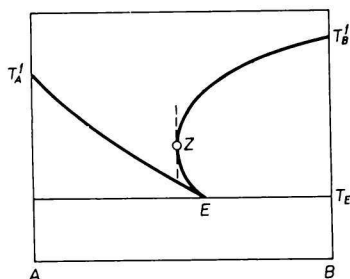
Fig. 4. Binary system A—B with a simple eutectic. The phenomenon of the retrograde solubility of the component B manifests itself in the part ZE on the liquidus curve of B.
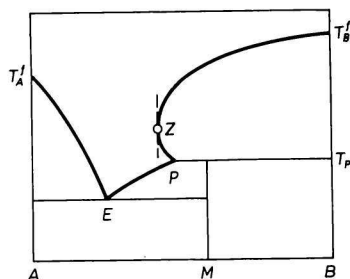
Fig. 5. Binary system A—B without solid solutions with an incongruently melting compound M. The retrograde solubility of the component B can be observed on the liquidus curve of this component.

$$\Delta \bar{H}_{M}^{1/0,s} \; k_{M}^{*} = \Delta \bar{H}_{B}^{1/0,s} \; k_{B}^{*} \qquad (13)$$

k_{M}^{*} and k_{B}^{*} are the slopes of tangents to the liquidus curves of substances M and B, respectively, in the point P in the system A—M. In Fig. 5, the system A—M forms a part of the system A—B. This transformation of the coordinates results in a change of the values of the slopes k_{i}^{*}, but not of their sign, i.e., if $k_{B}^{*} < 0$, then also $k_{B} < 0$, in the same peritectic point P. In the given case $\Delta \bar{H}_{M}^{1/0,s} > 0$, $k_{M}^{*} > 0$, $k_{B}^{*} < 0$, and consequently in agreement with eqn (13) also $\Delta \bar{H}_{B}^{1/0,s} = \Delta \bar{H}_{mix,B}^{1} + \Delta H_{B}^{0,1/0,s}$ must be smaller than zero. This result is again in agreement with the relation (11).

Finally, the relation for the course of liquidus curve as proposed by Ricci ([5], p. 82) should be discussed. For the i-th component it should hold

$$\frac{dx_i}{dT} = \frac{x_i L_i}{RT^2}, \qquad (14)$$

where L_i stands for the term $\Delta \bar{H}_{i}^{1/0,s} = \Delta \bar{H}_{mix,i}^{1} + \Delta H_{i}^{0,1/0,s}$ To analyze the particular relation (14), the generally valid eqn (11) will be used. If it held that $a_i^1 = x_i$ (i.e., in the case of classic ideal solution), then it would hold $(\partial \ln a_{eq,i}^1 / \partial x_i)_T = (1/x_i)_{eq}$ as it is the case in eqn (14), but simultaneously $\Delta \bar{H}_{mix,i}^1 = 0$. Hence the correct particular equation should be read

$$\left(\frac{dx_i}{dT} \right)_{eq} = \frac{x_i \, \Delta H_i^1}{RT^2} \qquad (15)$$

Consequently the form of eqn (14) is open to criticism.

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