Equilibrium "solidus—liquidus" in systems with limited solid solutions*

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An equation for the dependence of activities of a given substance in liquid and solid solutions on the temperature of primary crystallization of the substance was developed on the basis of the Planck function. The analysis of the course of the liquidus curve near the melting point of the pure substance shows that the objective difference between the calorimetrically and cryometrically determined values of the melting enthalpy of the discussed substance is a *sufficient* (though not *necessary*) condition for the existence of limited solid solutions.

На основании функции Планка было выведено уравнение для зависимости активностей данного вещества в жидком и твердом растворах от температуры первичной кристаллизации. Анализ хода кривых плавкости вблизи точки плавления чистого вещества показывает, что объективная разница между калориметрически и криометрически найденым значением энтальпии плавления, является *достаточным* (хотя и не *необходимым*) условием существования ограниченных твердых растворов в системе данного типа.

Even though the basic relations for the equilibrium in systems of the given type are known [1—3], so far no detailed analysis of the derivation of these relations seems to be performed, nor the course of the liquidus and solidus curves for high concentrations of the basic substances has been analyzed.

The dependence $f(a_i^l, a_i^s) = F(T_i)$ for systems of the given type

Let us consider a binary condensed system at $P = $ const in which limited solid solutions exist. For thermodynamic equilibrium in points "1" and "2" (Fig. 1) with respect to the component B, it holds

$$\bar{B}^l \rightleftarrows \bar{B}^s; \quad \bar{G}_B^l = \bar{G}_B^s$$

and thus also

$$\left[\frac{\bar{G}_B^l}{T} \right]_e = \left[\frac{\bar{G}_B^s}{T} \right]_{eq} \tag{1}$$

(In further considerations we omit the index "B".)

With an infinitesimal change of the independent variables T and P both sides of eqn (1) also change, *viz.*, the term on the left side by $d(\bar{G}^l/T)_{eq}$, that on the right side by $d(\bar{G}^s/T)_{eq}$. For equilibrium it again holds
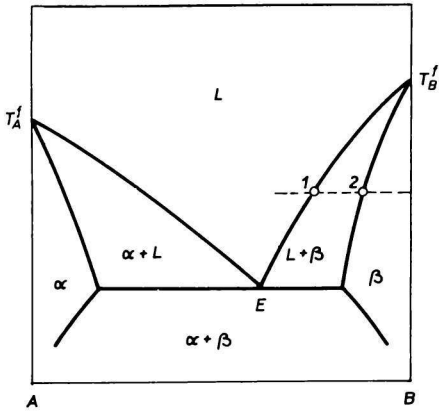
Fig. 1. Phase diagram of a binary condensed system A—B, in which the mutual limited solubility in the solid state of components occurs.

$$(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} + \mathrm{d}(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} = (\bar{G}^{\mathrm{s}}/T)_{\mathrm{eq}} + \mathrm{d}(\bar{G}^{\mathrm{s}}/T)_{\mathrm{eq}} \tag{2}$$

then with respect to eqn (1) the relation is valid

$$\mathrm{d}(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} = \mathrm{d}(\bar{G}^{\mathrm{s}}/T)_{\mathrm{eq}} \tag{3}$$

$$\bar{G}^{\mathrm{l}} = \mathrm{f}(T, x^{\mathrm{l}})_P ; \quad \bar{G}^{\mathrm{s}} = \mathrm{f}(T, x^{\mathrm{s}})_P ,$$

$$\mathrm{d}(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} = [\partial(\bar{G}^{\mathrm{l}}/T)/\partial T]_{P,x} \; \mathrm{d}T_{\mathrm{eq}} + [\partial(\bar{G}^{\mathrm{l}}/T)/\partial x]_{P,T} \cdot \mathrm{d}x_{\mathrm{eq}}$$

Choice of the standard states

Let us take as standard state the state of the pure undercooled substance B at the temperature T Thus if $x_{\mathrm{B}}^{\mathrm{l}} \to 1$, $a_{\mathrm{B}}^{\mathrm{l}} \to x_{\mathrm{B}}^{\mathrm{l}} \to 1$. The exact differential on the left side of eqn (3) can be further rearranged as follows

$$\mathrm{d}(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} = [\partial(G^{0,\mathrm{l}} + RT \ln a^{\mathrm{l}}/T)/\partial T]_{P,x} \; \mathrm{d}T_{\mathrm{eq}} +$$
$$+ [\partial(G^{0,\mathrm{l}} + RT \ln a^{\mathrm{l}}/T)/\partial x]_{P,T} \cdot \mathrm{d}x_{\mathrm{eq}} ,$$

$$\mathrm{d}(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} = [\partial(G^{0,\mathrm{l}}/T)/\partial T]_{P,x} \cdot \mathrm{d}T_{\mathrm{eq}} + R[\partial \ln a^{\mathrm{l}}/\partial T]_{P,x} \cdot \mathrm{d}T_{\mathrm{eq}} +$$
$$+ [\partial(G^{0,\mathrm{l}}/T)/\partial x]_{P,T} \cdot \mathrm{d}x_{\mathrm{eq}} + R[\partial \ln a^{\mathrm{l}}/\partial x]_{P,T} \cdot \mathrm{d}x_{\mathrm{eq}}$$

After applying the isobar equation we obtain

$$\mathrm{d}(\bar{G}^{\mathrm{l}}/T)_{\mathrm{eq}} = -\frac{H^{0,\mathrm{l}}}{T^2} \, \mathrm{d}T_{\mathrm{eq}} + R \, \mathrm{d} \ln a_{\mathrm{eq}}^{\mathrm{l}} \tag{3a}$$

as the equation holds

$$d \ln a^{l}(T, x)_{P} = [\partial \ln a^{l}/\partial T]_{P,x} \cdot dT + [\partial \ln a^{l}/\partial x]_{P,T} \cdot dx$$

Analogically we find that

$$d(\bar{G}^{s}/T)_{eq} = -\frac{H^{0,s}}{T^{2}} dT_{eq} + R \, d \ln a^{s}_{eq} \qquad (3b)$$

In this case the standard state of the pure solid substance B at the temperature T has been chosen. Thus it holds that if $x^{s}_{B} \to 1$, $a^{s}_{B} \to x^{s}_{B} \to 1$. Introducing the corresponding term from eqns $(3a)$ and $(3b)$ into eqn (3), we get

$$-(H^{0,l}/T^{2}) \, dT_{eq} + R \, d \ln a^{l}_{eq} = -(H^{0,s}/T^{2}) \, dT_{eq} + R \, d \ln a^{s}_{eq}$$

Rearranging,

$$d \ln (a^{l}/a^{s})_{eq} = (\Delta H^{0,l/0,s}/RT^{2}) \, dT_{eq} , \qquad (4)$$

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

Thus we have established the differential form of the fundamental equation

$$f(a^{l}_{i}, a^{s}_{i})_{eq} = F(T_{i})$$

By integrating eqn (4) we obtain

$$\int_{T}^{T^{t}} d \ln a^{l} - \int_{T}^{T^{t}} d \ln a^{s} = \int_{T}^{T^{t}} \frac{\Delta H^{0,l/0,s}}{RT^{2}} \cdot dT_{eq} \qquad (5)$$

Because both terms a^{l} and a^{s} equal one at T^{t}, the left side of eqn (4) becomes $-\ln (a^{l}/a^{s})$. Then rearranging eqn (5) we may write

$$-(\ln a^{l}/a^{s})_{eq} = \int_{T}^{T^{t}} \frac{\Delta H^{0,l/0,s}}{RT^{2}} \cdot dT_{eq} \qquad (6)$$

It holds further that

$$d \, \Delta H^{0,l/0,s} = \Delta C^{0,l/0,s}_{P} \, dT$$

Integrating this equation we find

$$\int_{T}^{T^{t}} d \, \Delta H^{0,l/0,s} = \Delta H^{0,l/0,s}_{T^{t}} - \Delta H^{0,l/0,s}_{T} = \int_{T}^{T^{t}} \Delta C^{0,l,0,s}_{P} \, dT$$

The quantity $\Delta H^{0,l/0,s}_{T^{t}}$ will be denoted by $\Delta H^{t} = $ const. Consequently,

$$\Delta H^{0,l/0,s}_{T} = \Delta H^{t} - \int_{T}^{T^{t}} \Delta C^{0,l/0,s}_{P} \, dT$$

Therefrom by substitution into eqn (6), integrating and rearranging we may write

$$\ln (a^{l}/a^{s})_{eq} = \frac{\Delta H^{t}}{R} \cdot (1/T^{t} - 1/T) + \frac{1}{RT} \int_{T}^{T^{t}} \frac{1}{T^{2}} \left[\int_{T}^{T^{t}} \Delta C^{0,l,0,s}_{P} \cdot dT \right] dT_{eq} \qquad (7)$$

Let us suggest that the molar heat capacity change may be represented by an equation of the form

$$\Delta C_P^{0,1/0,s} = \Delta a + \Delta bT + \Delta cT^{-2}$$

Then eqn (7) can be modified into the following form

$$\ln (a^l/a^s)_{eq} = (\Delta H^f/R)\ (1/T^f - 1/T) + (\Delta a/R)\ [T^f/T - 1 - \ln (T^f/T)] +$$

$$+ (\Delta b/2R)\ [(T^f)^2/T - 2T^f + T] + (\Delta c/2R)\ (1/T - 1/T^f)^2 \tag{8}$$

If $\Delta C_P^{0,1/0,s} = 0$, $a^s = 1$, we obtain the well-known generalized LeChatelier——Schröder equation for the course of liquidus curves in simple eutectic systems.

Regularities of the courses of the liquidus curves near the melting point of the pure component for systems of the given type

In this case, since the temperature interval $[T, T^f]$ is comparatively small (some °C only), we may neglect in eqn (8) all terms containing $\Delta C_P^{0,1/0,s}$ and we may write

$$\ln (a^l/a^s)_{eq} = (\Delta H^f/R)\ (1/T^f - 1/T) \tag{9}$$

Therefrom

$$\ln a^l_{eq} = (\Delta H^f/R)\ (1/T^f - 1/T) + \ln a^s_{eq} \tag{10}$$

The temperature dependence of the activity of the given component in the liquid phase may be expressed as follows

$$\ln a^l_{eq} = (\Delta H^*/R)\ (1/T^f - 1/T) \tag{11}$$

Evidently the term ΔH^* is of the same physical units as ΔH^f. By insertion from eqn (11) into eqn (10) it follows

$$(\Delta H^*/R)\ (1/T^f - 1/T) = (\Delta H^f/R)\ (1/T^f - 1/T) + \ln a^s$$

Multiplying by $R/(1/T^f - 1/T) = -RT^f/\Delta T$, where $\Delta T = T^f - T > 0$, this equation becomes

$$\Delta H^* = \Delta H^f - RT\, T^f\ \ln (a^s/\Delta T) \tag{12}$$

Eqn (12) also holds in the limiting case, if $x_i \to 1$. Then $a^l_i \to x^l_i \to 1$, $a^s_i \to x^s_i \to 1$, and

$$\lim \Delta H^* = \lim \Delta H^f - RT^f\ \lim (T \cdot \ln a^s/\Delta T) \tag{13}$$

Now we determine the limit values of all terms in eqn (13). From eqn (11) it follows

$$d \ln a' = da'/a' = (\Delta H^*/RT^2) \quad dT$$

Rearranging,

$$\Delta H^* = (RT^2/a') \quad (da'/dT) = (RT^2/a') \quad [1/(dT/da')]$$

and finally,

$$\lim_{x \to 1} \Delta H^* = R(T')^2/k_{a'}^0 \tag{14}$$

where

$$k_{a'}^0 = \lim_{x \to 1} (dT/da')$$

Consequently $k_{a'}^0$ is the slope of the tangent to the curve $a_i' = f(T_i)$ for $x_i \to 1$ in a system with solid solutions on the basis of the substance "i"

Let us consider the system B—C of the eutectic type, without any solid solutions of component C in the component B. Then for the component B it holds (Fig. 2)

$$\ln (a_{0,B}')_{eq} = (\Delta H'/R) \cdot (1/T' - 1/T) \tag{15}$$

Applying the same procedure as above, we obtain from eqn (15)

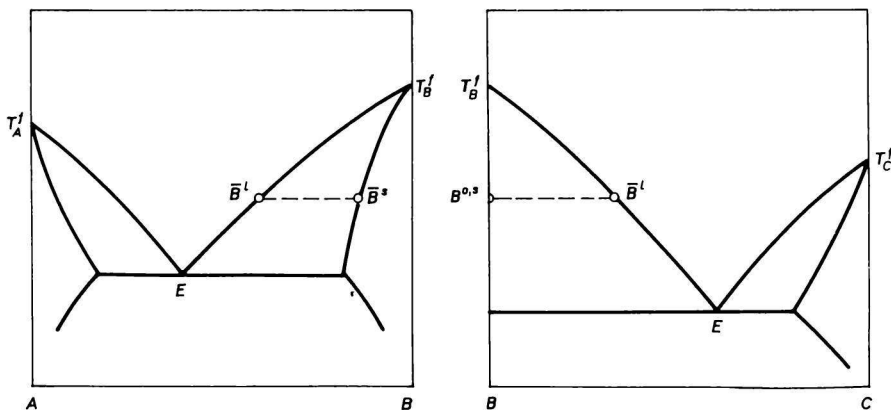$$\lim_{x_B \to 1} \Delta H' = R(T')^2/k^0 \tag{16}$$

where

Fig. 2. Comparison of the phase diagrams of the binary condensed systems A—B and B—C. The first of them exhibits a limited solid solution on the basis of the component B; in the second the solubility of the component C in the solid component B equals zero.

$$k^0{}_{a_0^!} = \lim_{x_B \to 1} (dT/da_0^!)$$

Consequently the term $k^0{}_{a_0^!}$ represents the slope of the tangent to the curve $a_i^! = f(T_i)$ for $x_i \to 1$ in a eutectic system, where no solid solutions are formed on the basis of the substance "i"

We still have to determine the term

$$\lim_{x \to 1} (T \cdot \ln a^s / \Delta T).$$

For $x \to 1$, $T \to T^f$, $a^s \to 1$, $\ln a^s \to 0$, $\Delta T = T^f - T \to 0$. We thus obtain an indefinite expression. To find its value the L'Hospital rule should be used

$$\lim_{x \to 1} (T \cdot \ln a^s / \Delta T) = T^f \lim_{x \to 1} (\ln a^s / \Delta T) =$$

$$= T^f \lim_{x \to 1} (1/a^s) \ [da^s/d(T^f - T)] = T^f \lim_{x \to 1} (1/a^s) \ [da^s/(-dT)] =$$

$$= -T^f \cdot \lim_{x \to 1} [1/(dT/da^s)] = -T^f \ (1/k_a^0{}_s) \,, \qquad (17)$$

where

$$k_a^0{}_s = \lim_{x \to 1} (dT/da^s)$$

Consequently $k_a^0{}_s$ is the slope of the tangent to the curve $a_i^s = f(T_i)$ for $x_i \to 1$ in a system in which solid solutions exist on the basis of the substance "i"

By substitution from eqns (14), (16), and (17) into eqn (13) we obtain

$$R(T^f)^2/k_a^0{}_! = R(T^f)^2/k_{a_0^!}^0 + R(T^f)^2/k_a^0{}_s$$

and dividing by $R(T^f)^2$

$$1/k_a^0{}_! = 1/k_{a_0^!}^0 + 1/k_a^0{}_s \,. \qquad (18)$$

Eqn (18) is the fundamental relation determining the course of the liquidus and solidus curves of the type $a_i = f(T_i)$ near the point $x_i = 1$.

Analogically to eqns (14) and (16) we formally may write

$$\lim_{x \to 1} \Delta H^s = R(T^f)^2/k_a^0{}_s \qquad (19)$$

Evidently ΔH^s has the same physical dimensions as ΔH^f.

With respect to the definition of the ΔH terms it holds

$$\lim_{x \to 1} \Delta H^* = \Delta H^* \qquad (20a)$$

$$\lim_{x \to 1} \Delta H^{\mathfrak{f}} = \Delta H^{\mathfrak{f}} \qquad (20b)$$

$$\lim_{x \to 1} \Delta H^{\mathfrak{s}} = \Delta H^{\mathfrak{s}} \qquad (20c)$$

Upon insertion from eqns (14), (16), and (19) into eqn (18) and with respect to eqns $(20a)$—$(20c)$ we easily find

$$\Delta H^* = \Delta H^{\mathfrak{f}} + \Delta H^{\mathfrak{s}} \qquad (21)$$

Inserting into eqn (11), we get for the vicinity of the point $x_i = 1$

$$\ln (a^{\mathfrak{l}})_{eq} = [(\Delta H^{\mathfrak{f}} + \Delta H^{\mathfrak{s}})/R] \ (1/T^{\mathfrak{f}} - 1/T) \qquad (22)$$

Comparison of eqns (9) and (15) gives the well-known relation

$$(a^{\mathfrak{l}})_{eq}/(a^{\mathfrak{s}})_{eq} = (a_0^{\mathfrak{l}})_{eq}$$

Eqn (21) can be obtained immediately from the modified eqn (9) if we write formally

$$\ln (a^{\mathfrak{s}})_{eq} = (\Delta H^{\mathfrak{s}}/R) \ (1/T^{\mathfrak{f}} - 1/T)$$

However, the experiments provide the dependence not of the type $T_i = f(a_i)$, but $T_i = f(x_i)$. Therefore we need to have the dependence $a_i = f(x_i)$ in a suitable form at our disposal. After a little modification we obtain from eqn (11)

$$T = \Delta H^*/(\Delta S^* - R \ln a^{\mathfrak{l}}) , \qquad (23)$$

where

$$\Delta S^* = \Delta H^*/T^{\mathfrak{f}}$$

By differentiating eqn (23) with respect to x we find

$$dT/dx = R \ \Delta H^* \ (a^{\mathfrak{l}})^{-1} \ (da^{\mathfrak{l}}/dx)/(\Delta S^* - R \ln a^{\mathfrak{l}})^2$$

and

$$\lim_{x \to 1} dT/dx = R \ \Delta H^* \ (\Delta S^*)^{-2} \ \lim_{x \to 1}(da^{\mathfrak{l}}/dx^{\mathfrak{l}}) =$$

$$= R(T^{\mathfrak{f}})^2/\Delta H^* \ \lim_{x \to 1}(da^{\mathfrak{l}}/dx^{\mathfrak{l}}) \qquad (24)$$

Let us take for the functional dependence $a_i = f(x_i)$ the so-called universal relationship [4], i.e.,

$$a_i = x_i^k \qquad (25)$$

For a not very great interval $[T, T']$ it holds with a sufficient accuracy that the exponent in eqn (25), viz., $k = \text{const} = k^{St}$; k^{St} being the Stortenbeker correction factor [4]. By differentiating eqn (25) with respect to x (we omit the index "i")

$$da/dx = k^{St} \; x^{(k^{St}-1)}$$

and

$$\lim_{x \to 1} (da/dx) = k^{St} \tag{26}$$

Therefore it holds

$$\Delta H^* = [R(T')^2/k^0_{x'}] \; k^{St,l} \tag{27}$$

($k^{St,l}$ is related to the activity of the given substance in the liquid solution.)

Analogically we find that

$$\Delta H^l = [R(T')^2/k^0_{x\delta}] \; k^{St,l} \tag{28}$$

and finally

$$\Delta H^s = [R(T')^2/k^0_{x^s}] \; k^{St,s} \tag{29}$$

($k^{St,s}$ is related to the activity of the given substance in the solid solution.)

Generally,

$$k^{St,l} \neq k^{St,s}$$

By comparison of eqn (21) with eqns $(27$—$29)$ we obtain

$$k^{St,l}/k^0_{x'} = k^{St,l}/k^0_{x\delta} + k^{St,s}/k^0_{x^s} \tag{30}$$

and if $k^{St,l} = k^{St,s}$

$$1/k^0_{x'} = 1/k^0_{x\delta} + 1/k^0_{x^s} \tag{31}$$

It follows from eqn (30) that

$$1/k^0_{x^s} = (k^{St,l}/k^{St,s}) \; (k^0_{x\delta} - k^0_{x'})/k^0_{x\delta} \; k^0_{x'} \tag{32}$$

or rearranging,

$$k^0_{x^s} = (k^{St,s}/k^{St,l}) \; k^0_{x\delta} \; k^0_{x'}/(k^0_{x\delta} - k^0_{x'}) \tag{33}$$

Always it holds that

$$k^0_{x'} \leqslant k^0_{x\delta}$$

Substitution from eqn (32) into eqn (29) yields

$$\Delta H^s = R(T')^2 \; k^{St,l} \; (k^0_{x\delta} - k^0_{x'}/k^0_{x\delta} \cdot k^0_{x'}) \tag{34}$$
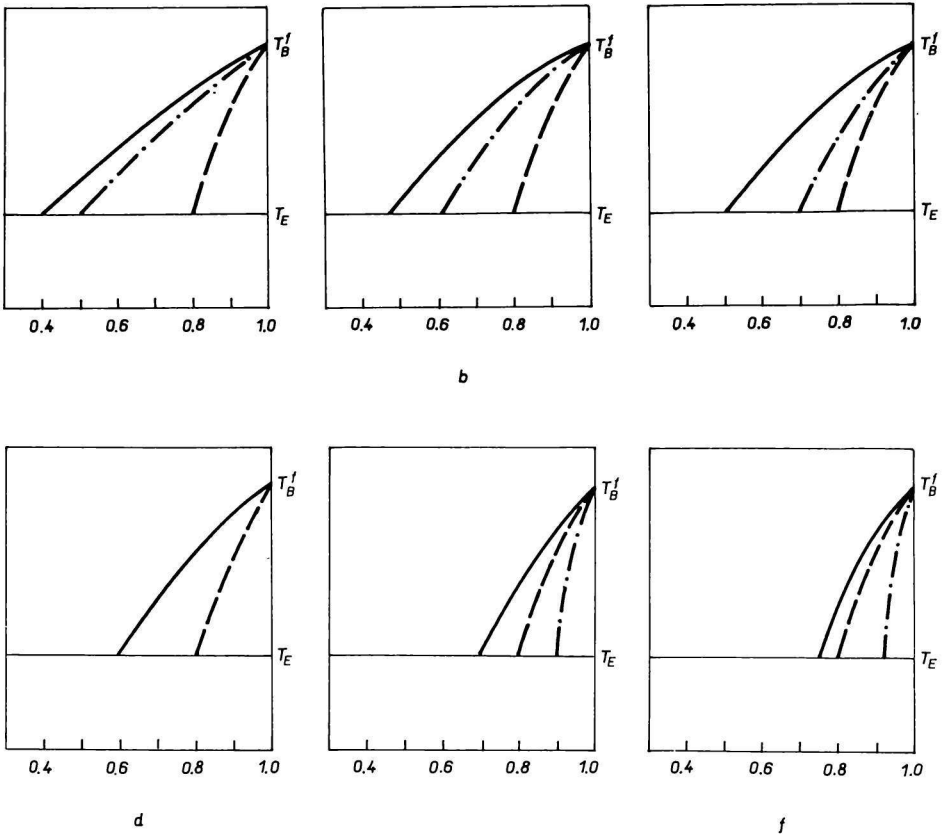
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Fig. 3. Schematic comparison of the course of the curves of liquidus (———) and solidus (— · — · —) of the component B in a system with limited solid solutions on the basis of B, and the course of the liquidus curve (— — — —) of the same B in simple eutectic system. The mole fractions characterizing the course of these curves at a chosen temperature T_B are given:

a) $x^l = 0.40$, $x^s = 0.50$; b) $x^l = 0.48$, $x^s = 0.60$; c) $x^l = 0.56$, $x^s = 0.70$; d) $x^l = 0.64$, $x^s = 0.80$; e) $x^l = 0.72$, $x^s = 0.90$; f) $x^l = 0.76$, $x^s = 0.95$.

In all cases $x_0^l = 0.80$.

$$0 \leqslant \Delta H^s$$

It follows from eqn (34) that for the determination of ΔH^s we need not know the value of $k^{St,s}$

Formally we may write

$$\ln (x^s)^{k^{St,s}} = (\Delta H^s / R) \ (1/T^f - 1/T)$$

Therefrom after modification and using eqn (34)

$$\ln x^s = k^{St,l} \ (T^f)^2 \ (k_{x_0^l}^0 - k_{x^l}^0)/k^{St,s} \ k_{x_0^l}^0 \ k_{x^l}^0 \ (1/T^f - 1/T) \qquad (35)$$

Rearranging eqn (28) we get

$$k^{St,l} = \Delta H^f \; k_{x_0}^0 / R(T^f)^2$$

Insertion of $k^{St,l}$ from this relation into eqn (35) gives

$$\ln x^s = \Delta H^f \; (k_{x_0}^0 - k_{x^l}^0)/R \; k_{x^l}^0 \cdot k^{St,s} \; (1/T^f - 1/T) \qquad (36)$$

The relation (36) may be used in calculating the course of solidus curve near the melting point of pure substances in systems of the given type.

Fig. $3a$—$3f$ show some cases of the course of the curves x^l, x_0^l and x^s provided that $k^{St,l} = k^{St,s} = 1$ and $x_0^l = 0.8$ at a chosen temperature T_B.

Practical use of the deduced relations

From the data for the liquidus curve of systems in which we search for limited solid solutions we determine the slope $k_{x^l}^0$ and using eqn (14) the value of the quantity ΔH^*. If the difference $\Delta H^* - \Delta H^f$ is greater than the admissible error in measurement (ΔH^f being determined calorimetrically or cryometrically from the course of the liquidus curve of the given substance in systems of the eutectic type in which on the basis of the discussed substance no solid solutions are formed) then it is a sufficient evidence of the presence of limited solid solutions in the system. If the above-mentioned difference is equal to zero (exactly or within the limits of experimental errors), the presence of solid solutions in the studied system cannot be determined definitely in the described way. In this case the slope of the tangent to the solidus curve for $x \to 1$, viz., $k_{x^s}^0 \to \infty$ (Fig. 4). Then it follows from eqn (31) that $k_{x^l}^0$ equals $k_{x_0}^0$ and hence $\Delta H^* = \Delta H^f$. In such a case the existence of limited solid solutions has to be proved by other methods.
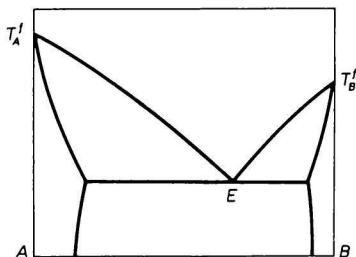

Fig. 4. Phase diagram of a binary condensed system A—B. On the side of the component A the criterion for the existence of limited solid solutions fails.

In deducing all the relations the formation of associates of the type *e.g.*, A_n—B, where $n > 1$, has not been taken into consideration. Therefore the relations cannot be generally used if the components form associated molecules or particles in the solutions.

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