

**Thermodynamics of phase equilibria
in the systems with polymorphic transitions**
**IV.* Systems having in high temperature subsolidus region
continuous solid solutions but forming no compounds**

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Thermodynamics of phase equilibria in the binary condensed systems which form with respect to "solidus—liquidus" equilibrium continuous solid solutions and which have in the subsolidus region polymorphic modifications of components is discussed. The polymorphic modifications can form either no solid solutions, either limiting or continuous solid solutions.

Rules describing the course of curves of monovariant phase equilibrium in the vicinity of eutectoid points were derived assuming classical ideal behaviour of all solid solutions taking part in the equilibrium. Also the rules which should be obeyed by the slopes of tangents to the curves of monovariant phase equilibrium of continuous solid solutions in subsolidus region are presented.

Были изучены двойные конденсированные системы, в которых существуют с точки зрения равновесия «солидус—ликвидус» неограниченные твердые растворы и в области под солидусом образуются полиморфные модификации компонентов, взаимно полностью, ограниченно или неограниченно растворимые.

Получены закономерности хода кривых моновариантного фазового равновесия в окрестности эвтектоидных точек при условии классически идеального поведения всех твердых растворов, участвующих в указанном равновесии, а также закономерности для наклона касательных кривых моновариантного фазового равновесия для неограниченных твердых растворов в области под солидусом.

For the systems of this type it is not important if the course of liquidus and solidus curves is a monotonous one or if there is maximum or minimum on the curves.

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1. One component exists in two polymorphic modifications

In the simplest case only low temperature modification of one of the two components, e.g. of component B (Fig. 1) is formed in the subsolidus region. Along the curve (T^{α} , F) the following equilibrium takes place



In this equilibrium two phases coexist, viz. the continuous solid solution and pure component B in the form of low temperature modification. Thus according to Gibbs phase rule $F = C - Ph + 1 = 2 - 2 + 1 = 1$ and, therefore, the temperature of polymorphic transition $T^{\alpha}(B_1/B_2)$ is not constant. The equation of monovariant curve (T^{α} , F) has the form

$$\ln \alpha^{\alpha}(B_1) = \frac{\Delta H^{\alpha}(B_1/B_2)}{R} \left[\frac{1}{T^{\alpha}(B_1/B_2)} - \frac{1}{T} \right] \quad (2)$$

It follows that it is formally identical with the LeChatelier—Shreder equation. By a cryometric treatment of the curve (T^{α} , F) one can determine the numerical value of the quantity $\Delta H^{\alpha}(B_1/B_2)$.

When we cool a system we often observe that not the pure component $B_2^{0,\alpha}$ but a limiting solid solution formed on the basis of this component is separated (Fig. 2). In this case it holds for the phase equilibrium

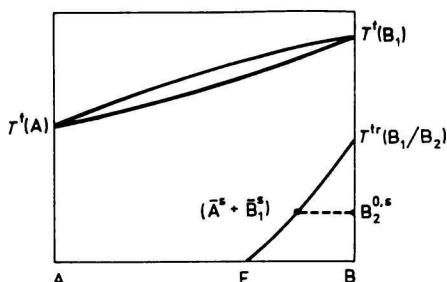


Fig. 1. Phase diagram of the condensed system A—B₁(B₂) with continuous liquid and solid solutions. Pure low temperature polymorphic modification B₂^{0,α} of component B is in equilibrium with solid solution (A^α + B₁^α).

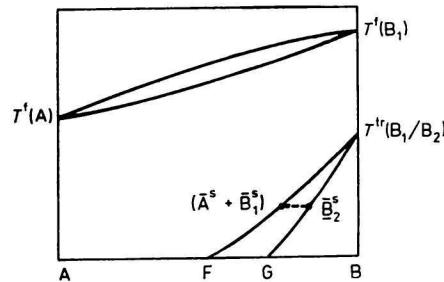
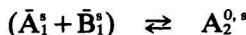


Fig. 2. Phase diagram of the condensed system A—B₁(B₂) with continuous liquid and solid solutions. Limiting solid solution formed on the basis of low temperature polymorphic modification B₂^α of component B is in equilibrium with solid solution (A^α + B₁^α).

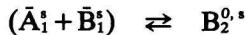
2. Both components of the system can exist in polymorphic modifications

- a) Only pure solid components exist in the subsolidus region

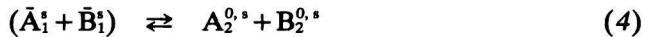
Let us assume that in subsolidus region polymorphic modifications of both components can be formed and that transition temperature T^α decrease in both cases. If the low temperature modifications of components are completely immiscible we get a phase diagram illustrated in Fig. 3. Along the curve $[T^\alpha(A_1/A_2), \epsilon]$ the following phase equilibrium exists



and along the curve $[T^\alpha(B_1/B_2), \epsilon]$ it holds



Nonvariant equilibrium is then established in the eutectoid point. It holds



Therefore when we take heat from the system pure low temperature modification of the component $A_2^{0,s}$ is formed along the curve $[T^\alpha(A_1/A_2), \epsilon]$ while along the curve $[T^\alpha(B_1/B_2), \epsilon]$ it is the pure low temperature modification of component $B_2^{0,s}$. At the eutectoid point ϵ the continuous solid solution splits into pure substances $A_2^{0,s}$ and $B_2^{0,s}$.

Each curve $[T^\alpha(A_1/A_2), \epsilon]$, $[T^\alpha(B_1/B_2), \epsilon]$ can be described by an equation of the type (2). For the slopes of tangents to these curves of monovariant equilibrium we can apply at the point ϵ the rule which is similar to CTC II [1—3]. This rule can be derived easily for the case when the solid solution $(\bar{A}_1^s + \bar{B}_1^s)$ behaves ideally or if it is not far from ideality. Differential form of the equation of the curve of monovariant equilibrium $[T^\alpha(A_1/A_2), \epsilon]$ is

$$d \ln x^s(A_1) = \frac{\Delta H^\alpha(A_1/A_2)}{RT^2} \cdot dT \quad (5)$$

which can be also written as

$$\frac{dx^s(A_1)}{x^s(A_1)} = \frac{\Delta H^\alpha(A_1/A_2)}{RT^2} \cdot dT \quad (6)$$

Multiplying eqn (6) by

$$\frac{x^s(A_1)}{dx^s(A_1)} \cdot RT^2$$

yields

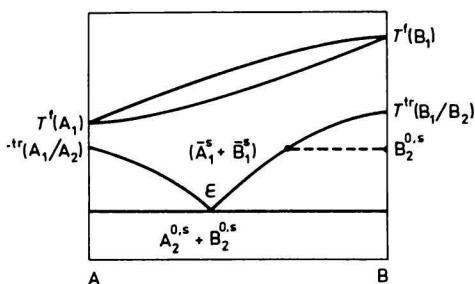


Fig. 3. Phase diagram of the condensed system $A_1(A_2)-B_1(B_2)$ with continuous liquid and solid solutions. Low temperature polymorphic modifications of both components are completely immiscible. There is one simple eutectoid point in the subsolidus region of the phase diagram.

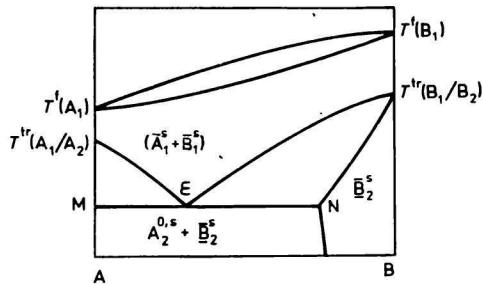


Fig. 4. Phase diagram of the condensed system $A_1(A_2)-B_1(B_2)$ with continuous liquid and solid solutions. The low temperature pure polymorphic modification $A_2^{0,s}$ of component A is in equilibrium with limiting solid solution formed on the basis of low temperature polymorphic modification of component B. There is one eutectoid point in the subsolidus region.

$$RT^2 = x^*(A_1) \cdot \Delta H^r(A_1/A_2) \cdot \frac{dT}{dx^*(A_1)}$$

which can be written as

$$RT^2 = x^*(A_1) \cdot \Delta H^r(A_1/A_2) \cdot k^*(A_1) \quad (7)$$

$k^*(A_1)$ is the slope of tangent to the curve $[T^r(A_1/A_2), \varepsilon]$. Similarly for the component B we obtain

$$RT^2 = x^*(B_1) \cdot \Delta H^r(B_1/B_2) \cdot k^*(B_1) \quad (8)$$

Both curves of monovariant equilibrium intersect at temperature $T(\varepsilon)$. In this case the product RT^2 can be eliminated from eqns (7) and (8) which results in

$$x^*(A_1) \cdot \Delta H^r(A_1/A_2) \cdot k^*(A_1) = x^*(B_1) \cdot \Delta H^r(B_1/B_2) \cdot k^*(B_1) \quad (9)$$

where

$$x^*(A_1) + x^*(B_1) = 1$$

Eqn (9) is a modified form of the CTC II.

- b) In the subsolidus region limiting solid solutions are formed

Another case occurs when instead of pure component a limiting solid solution formed either on one side (Fig. 4) or on both sides (Fig. 5) coexists with the continuous solid solution ($\bar{A}_1^s + \bar{B}_1^s$). Then for the component A of the phase

diagram given in Fig. 4 the relations (5—7) are valid. For the component B (Fig. 4) it holds (assuming that the continuous solid solution $(\bar{A}_1^s + \bar{B}_1^s)$ as well as the limiting solid solution \bar{B}_2^s are ideal)

$$d \ln \frac{x^s(B_1)}{x^s(B_2)} = \frac{\Delta H^\nu(B_1/B_2)}{RT^2} \cdot dT \quad (10)$$

which can be rewritten as

$$d \ln x^s(B_1) - d \ln x^s(B_2) = \frac{\Delta H^\nu(B_1/B_2)}{RT^2} \cdot dT \quad (11)$$

$$\frac{dx^s(B_1)}{x^s(B_1)} - \frac{dx^s(B_2)}{x^s(B_2)} = \frac{\Delta H^\nu(B_1/B_2)}{RT^2} \cdot dT \quad (12)$$

It should be emphasized that $dx^s(B_1) \neq dx^s(B_2)$ despite of the fact that both expressions are infinitesimal quantities. In this case it is easy to prove that $dx^s(B_1) > dx^s(B_2)$.

$$\frac{x^s(B_2) \cdot dx^s(B_1) - x^s(B_1) \cdot dx^s(B_2)}{x^s(B_1) \cdot x^s(B_2)} = \frac{\Delta H^\nu(B_1/B_2)}{RT^2} \cdot dT \quad (13)$$

We multiply eqn (13) by $x^s(B_1) \cdot x^s(B_2) \cdot RT^2/dT$ which gives

$$\begin{aligned} RT^2 \left[x^s(B_2) \cdot \frac{dx^s(B_1)}{dT} - x^s(B_1) \cdot \frac{dx^s(B_2)}{dT} \right] &= \\ &= x^s(B_1) \cdot x^s(B_2) \cdot \Delta H^\nu(B_1/B_2) \end{aligned} \quad (14)$$

The expressions $dT/dx^s(B_1)$ and $dT/dx^s(B_2)$ correspond to the slopes of tangents to the curves $[T^\nu(B_1/B_2), \varepsilon]$ and $[T^\nu(B_1/B_2), N]$, respectively. We shall denote them as $k^s(B_1)$ and $k^s(B_2)$. Then it holds

$$RT^2 [x^s(B_2)/k^s(B_1) - x^s(B_1)/k^s(B_2)] = x^s(B_1) \cdot x^s(B_2) \cdot \Delta H^\nu(B_1/B_2)$$

or

$$RT^2 \cdot \frac{x^s(B_2) \cdot k^s(B_2) - x^s(B_1) \cdot k^s(B_1)}{k^s(B_1) \cdot k^s(B_2)} = x^s(B_1) \cdot x^s(B_2) \cdot \Delta H^\nu(B_1/B_2)$$

Then it follows

$$RT^2 = \frac{x^s(B_1) \cdot k^s(B_1) \cdot x^s(B_2) \cdot k^s(B_2)}{x^s(B_2) \cdot k^s(B_2) - x^s(B_1) \cdot k^s(B_1)} \cdot \Delta H^\nu(B_1/B_2) \quad (15)$$

At temperature $T = T(\varepsilon)$ the left and right side of eqns (7) and (15) are equal and thus it holds

$$x^*(A_1) \cdot k^*(A_1) \cdot \Delta H^r(A_1/A_2) = \\ = \frac{x^*(B_1) \cdot k^*(B_1) \cdot x^*(B_2) \cdot k^*(B_2)}{x^*(B_2) \cdot k^*(B_2) - x^*(B_1) \cdot k^*(B_1)} \cdot \Delta H^r(B_1/B_2) \quad (16)$$

The relationship (16) describes the rule which must be obeyed by the slopes of tangents to the curves of monovariant equilibrium at the eutectoid point ϵ if one-side solid solution is formed in subsolidus region (Fig. 4). When solid solutions are formed on both sides of the system then it holds for the slopes of tangents to curves at the point ϵ that

$$\frac{x^*(A_1) \cdot k^*(A_1) \cdot x^*(A_2) \cdot k^*(A_2)}{x^*(A_2) \cdot k^*(A_2) - x^*(A_1) \cdot k^*(A_1)} \cdot \Delta H^r(A_1/A_2) = \\ = \frac{x^*(B_1) \cdot k^*(B_1) \cdot x^*(B_2) \cdot k^*(B_2)}{x^*(B_2) \cdot k^*(B_2) - x^*(B_1) \cdot k^*(B_1)} \cdot \Delta H^r(B_1/B_2) \quad (17)$$

As we have shown above the relationships (16) and (17) are valid in that case when all solid solutions coexisting in equilibrium at temperature $T(\epsilon)$ are ideal.

Eqns (9), (16), and (17) are special cases of the CTC II, which was modified for subsolidus equilibria.

General solution of the CTC II for "solidus—liquidus" equilibrium has been derived in a different way by Hagège [4]. Practical value of the relationships (16) and (17) consists in that they allow to calculate one from the quantities $\Delta H^r(A_1/A_2)$ or $\Delta H^r(B_1/B_2)$ providing the other data are known. The relationships can be used also for verification of consistency of experimental data.

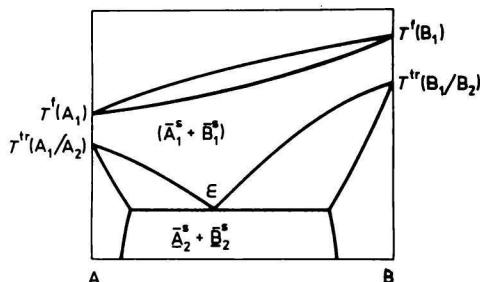


Fig. 5. Phase diagram of the condensed system $A_1(A_2)-B_1(B_2)$ with continuous liquid and solid solutions of high temperature polymorphic modifications of both components A and B. In subsolidus region limiting solid solutions formed on the basis of low temperature polymorphic modifications of components A and B coexist in equilibrium. There is one eutectoid point in this phase diagram.

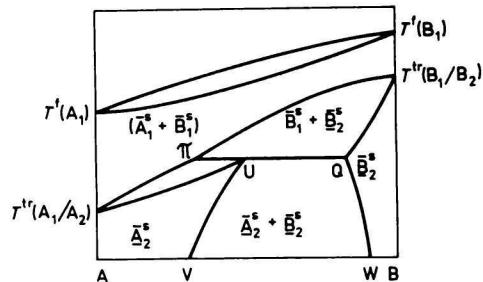


Fig. 6. Phase diagram of the condensed system $A_1(A_2)-B_1(B_2)$ with continuous liquid and solid solutions formed by high temperature polymorphic modifications of both components A and B. Low temperature modifications of these components have only limiting miscibility. There is one peritectoid point in the subsolidus region.

If the temperature of polymorphic modification T^{tr} of a given component increases as a result of addition of the other component then we observe in the phase diagram a peritectoid point (Fig. 6). There are phase diagrams which have in the subsolidus region both eutectoid and peritectoid points (Fig. 7).

For parts of the binodal curve (V, U) and (W, Q) (Figs. 6 and 7) we can write according to *Tamman* [5] a simple logarithmic relation

$$\ln x(i) = a + b/T$$

From the shape of this expression one can presume that the equation of binodal curve is formally similar to the LeChatelier—Shreder equation.

c) Continuous solid solutions are formed in the subsolidus region

We shall study phase diagrams of the type illustrated in Fig. 8. Using the method of four-term isothermal-isobaric ΔG cycle [6] we obtain the following relationships

$$\ln \frac{a^*(A_1)}{a^*(A_2)} = \frac{\Delta H^{\text{tr}}(A_1/A_2)}{R} \cdot \left[\frac{1}{T^{\text{tr}}(A_1/A_2)} - \frac{1}{T} \right] \quad (18)$$

$$\ln \frac{a^*(B_1)}{a^*(B_2)} = \frac{\Delta H^{\text{tr}}(B_1/B_2)}{R} \cdot \left[\frac{1}{T^{\text{tr}}(B_1/B_2)} - \frac{1}{T} \right] \quad (19)$$

The relationships (18) and (19) hold exactly under the assumption that ΔH^{tr} does not depend on temperature. This simplification is fulfilled satisfactorily when

$$|T^{\text{tr}}(B_1/B_2) - T^{\text{tr}}(A_1/A_2)| < 100 \text{ K}$$

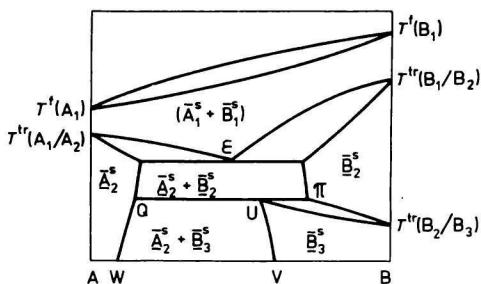


Fig. 7. Phase diagram of the condensed system $A_1(A_2)-B_1(B_2, B_3)$ with continuous liquid and solid solutions of high temperature polymorphic modifications of both components A and B. Pairs of the polymorphic modifications A_2 and B_2 and of A_2 and B_3 , respectively, have only limiting mutual miscibility. In the subsolidus region there is one eutectoid and one peritectoid point; $T(\pi) < T(E)$.

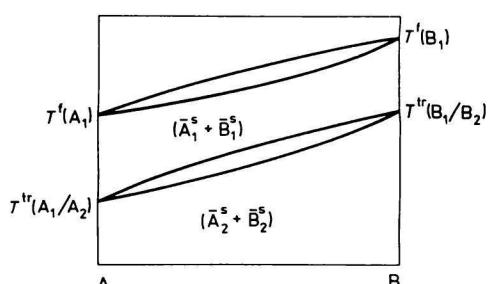


Fig. 8. Phase diagram of the condensed system $A_1(A_2)-B_1(B_2)$ with continuous liquid and solid solutions of high temperature polymorphic modifications of both components A and B. In the subsolidus region continuous solid solutions $(\bar{A}_1^s + \bar{B}_1^s)$ coexist in equilibrium with continuous solid solutions $(\bar{A}_2^s + \bar{B}_2^s)$.

If the solid solutions are ideal it holds that $a(i) = x(i)$ and because $x(i) + x(j) = 1$ we get

$$\ln \frac{x^*(A_1)}{x^*(A_2)} = \frac{\Delta H^\text{r}(A_1/A_2)}{R} \cdot \left[\frac{1}{T^\text{r}(A_1/A_2)} - \frac{1}{T} \right] \quad (20)$$

$$\ln \frac{1-x^*(A_1)}{1-x^*(A_2)} = \frac{\Delta H^\text{r}(B_1/B_2)}{R} \cdot \left[\frac{1}{T^\text{r}(B_1/B_2)} - \frac{1}{T} \right] \quad (21)$$

Let us introduce new variables

$$x^*(A_1)/x^*(A_2) = M; \quad [1-x^*(A_1)]/[1-x^*(A_2)] = Q$$

Then we can write

$$x^*(A_1) = f_1(T) = \frac{1-Q}{M-Q} \cdot M \quad (22)$$

$$x^*(A_2) = f_2(T) = \frac{1-Q}{M-Q} \quad (23)$$

$$x^*(B_1) = f_3(T) = \frac{M-1}{M-Q} \cdot Q \quad (24)$$

$$x^*(B_2) = f_4(T) = \frac{M-1}{M-Q} \quad (25)$$

Further we can determine the slopes of tangents to the curves of monovariant phase equilibrium in the subsolidus region [7] for $x(A) \rightarrow 1$ or for $x(B) \rightarrow 1$

$$k^{0,*}(A_1/A_2) = \frac{R \cdot [T^\text{r}(A_1/A_2)]^2}{\Delta H^\text{r}(A_1/A_2)} \cdot \frac{q-1}{q} \quad (26)$$

$$k^{0,*}(A_1/A_2) = \frac{R \cdot [T^\text{r}(A_1/A_2)]^2}{\Delta H^\text{r}(A_1/A_2)} \cdot q - 1 \quad (27)$$

$$k^{0,*}(B_1/B_2) = \frac{R \cdot [T^\text{r}(B_1/B_2)]^2}{\Delta H^\text{r}(B_1/B_2)} \cdot \frac{m-1}{m} \quad (28)$$

$$k^{0,*}(B_1/B_2) = \frac{R \cdot [T^\text{r}(B_1/B_2)]^2}{\Delta H^\text{r}(B_1/B_2)} \cdot m - 1 \quad (29)$$

For the quantities m and q it holds

$$\ln m = \frac{\Delta H^\text{r}(A_1/A_2)}{R} \cdot \left[\frac{1}{T^\text{r}(A_1/A_2)} - \frac{1}{T^\text{r}(B_1/B_2)} \right] \quad (30)$$

$$\ln q = \frac{\Delta H^\text{r}(B_1/B_2)}{R} \cdot \left[\frac{1}{T^\text{r}(B_1/B_2)} - \frac{1}{T^\text{r}(A_1/A_2)} \right] \quad (31)$$

From eqns (26) and (27) we found that

$$k^{0,\circ}(A_1/A_2)/k^{0,\circ}(A_1/A_2) = 1/q \quad (32)$$

From eqns (28) and (29) it follows further that

$$k^{0,\circ}(B_1/B_2)/k^{0,\circ}(B_1/B_2) = 1/m \quad (33)$$

It should be stressed that eqns (32) and (33) hold not only for ideal but also for real solid solutions. The solutions must be, however, of the first kind, i.e. it must hold that

$$\lim_{x(i) \rightarrow 1} \frac{da(i)}{dx(i)} = 1 \quad (34)$$

If eqn (34) fulfilled eqns (32) and (33) have the character of criteria of thermodynamic consistency for the course of curves of monovariant phase equilibrium of polymorphic modifications in the subsolidus region.

Practical validity of these equations consists in that they allow to calculate from the course of curves of monovariant equilibrium the enthalpies of modification transitions. Thus from the curve measured in the vicinity of the point $T^{\text{tr}}(A_1/A_2)$ (viz. for $x(A) \rightarrow 1$) it is possible to calculate the quantity $\Delta H^{\text{tr}}(B_1/B_2)$ of the reaction $B_2^{0,\circ} \rightarrow B_1^{0,\circ}$ at the point $T^{\text{tr}}(B_1/B_2)$ (viz. for $x(B) \rightarrow 1$).

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