Thermodynamics of phase equilibria in the systems with polymorphic transitions
II. Systems in which complex compounds are formed but solid solutions are not present

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Thermodynamic analysis of the equilibrium "solidus—liquidus" in binary condensed systems having no solid solutions in which, however, congruently or incongruently melting complex compounds are formed is presented. It is assumed that components or constituents of the system can undergo several polymorphic phase transitions of the enantiotropic type.

The course of liquidus curves in the vicinity of remarkable points of the systems of this type is determined by four criteria of thermodanymic consistency (CTC I—IV).

Было осуществлено термодинамическое рассмотрение равновесий «солидус—ликвидус» в двойных конденсированных системах без твердых растворов, содержащих комплексные соединения с конгруэнтной и инконгруэнтной точкой плавления. При компонентах или составляющих систем предполагается образование полиморфных фазовых переходов энантиотропного характера.

Ход кривых ликвидуса в окрестности характеристических точек систем этого типа определяется критериями термодинамической конзистентности (КТК I—IV).

1. Systems with congruently melting compound which thermally partially dissociates. It is assumed that the compound can exist in two polymorphic modifications

Let us assume that in the system A—B a complex compound $Z = A_p B_q$ is formed and that this compound undergoes a partial thermal dissociation. For the slope of tangent $k^0(1/A)$ to the liquidus curve of the component A in its melting point it holds

$$k^0(1/A) = \lim_{x(A) \to 1} \frac{dT(A)}{dx(A)} = \frac{R \cdot [T^t(A)]^2}{\Delta H^t(A)} \cdot \lim_{x(A) \to 1} \frac{da(A)}{dx(A)} \qquad (1)$$

which can be rewritten as

$$k^0(1/A) = \frac{R \cdot [T^f(A)]^2}{\Delta H^f(A)} \cdot k^{St}(Z/A) \tag{2}$$

The symbols in these equations have the following meaning:

$T(A)$ is the liquidus temperature of the component A,

$x(A)$ is the mole fraction of the component A in the subsystem A—Z,

$T^f(A)$ is the temperature of fusion of pure substance A,

R is the gas constant,

$\Delta H^f(A)$ is the molar enthalpy of fusion of pure substance A,

$k^{St}(Z/A)$ is the Stortenbeker's factor which equals the number of new species which appear in the molten component A as a result of addition of one molecule of the substance Z.

Eqn (2) holds regardless of the shape of the functional dependence $a(A) = \mathrm{f}[x(A)]$. We denote this equation as the CTC I [1].

The quantity $k^{St}(Z/A)$ depends generally on the degree of thermal dissociation of compound Z. We shall denote this degree of dissociation as b and its limiting values as

$$\lim_{x(Z) \to 1} b = b_0; \quad \lim_{x(Z) \to 0} b = b_\infty$$

At infinite dilution (*i.e.* when $x(Z) \to 0$) one "weighed in" molecule of compound Z yields: $(1 - b_\infty)$ molecules of undissociated compound Z, pb_∞ molecules of the substance A, and qb_∞ molecules of the substance B. As new species with respect to the substance A are to be considered the species Z and B the total number of which is $1 + (q-1) b_\infty = k^{St}(Z/A)$. If $q = 1$ then $k^{St}(Z/A) = 1$. In all other cases $k^{St}(Z/A) \neq 1$. It follows that from the slope of tangent $k^0(1/A)$ we can determine the quantity b_∞ and consequently also b_0 because the quantities b_∞ and b_0 are connected by a functional dependence [2].

The circumstance that $k^{St}(Z/A)$ does not necessarily equal to one must be taken into account at the application of the cryometric method to the analysis of the course of liquidus curve of the substance A in the vicinity of $T^f(A)$.

From Fig. 1 it follows that the slope of tangent $k^0(1/Z_1)$ to the liquidus curve of compound Z equals zero. Therefore it is not possible to carry out the cryometric method on the basis of the substance Z. The same is true also for the slope $k^0(1/Z_2)$.

The course of the liquidus curves of substances A and Z_2 in the vicinity of eutectic point E is described by the CTC II [1, 3, 4].

$$x(A) \cdot \Delta \bar{H}^{f/0, s}(A) \cdot k(1/A) = x(Z). \Delta \bar{H}^{f/0, s}(Z_2) \cdot k(1/Z_2) \tag{3}$$

All quantities in eqn (3) are related to composition and temperature of the eutectic point E_1. In those cases when the system is not very far from ideal behaviour and
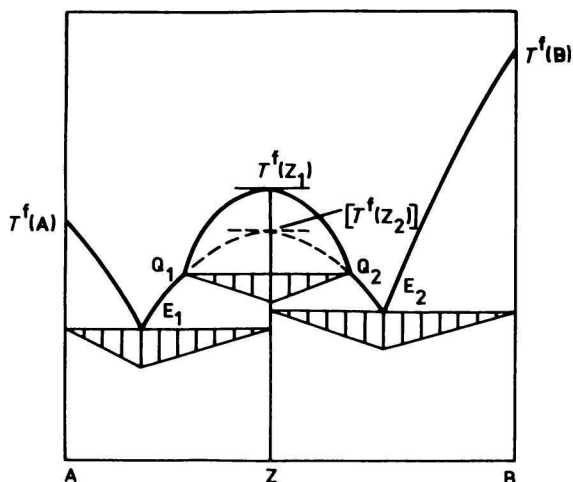
Fig. 1. Phase diagram of the condensed system A—B in which a complex congruently melting compound Z is formed. No solid solutions are present. Both the high temperature polymorphic modification of this compound Z_1 and its low temperature modification Z_2 partially thermally dissociate at melting temperature.

when the differences $T^f(A) - T(E_1)$ and $T^f(Z_1) - T(E_1)$ are not too great (less than 100 K) we can use a simplified relation

$$x(A) \cdot \Delta H^f(A) \cdot k(1/A) = x(Z) \cdot \Delta H^f(Z_2) \cdot k(1/Z_2) \qquad (4)$$

The course of liquidus curve of modifications Z_1 and Z_2 is in the vicinity of the point Q described by the CTC III [1].

Till now we have discussed the system A—Z where $Z = A_pB_q$ and the component A is one of the products of partial thermal dissociation of Z. The obtained results can be easily extended to the case of the system C—Z in which the component C does not belong to products of dissociation of the compound Z. In this case, all species resulting from dissociation of Z represent from the point of view of the substance C new species and therefore it holds

$$k^{St}(Z/C) = 1 + (p+q-1) \cdot b_\infty \qquad (5)$$

If the system C—Z has character of a quasi-binary system (Fig. 2) then it is in principle possible to determine by means of the cryometric method realized on the basis of substance C the quantity b_∞ and therefore also b and b_0. In comparison with the preceding case the shape of liquidus curves of the compound Z will change so that $0 < k^0(1/Z_2) < k^0(1/Z_1)$. Thus in this case the cryometric method can be carried out also on the basis of the substance Z. When we compare the composition coordinate of the point Q in systems of the type C—Z, D—Z, *etc.*, we find that it
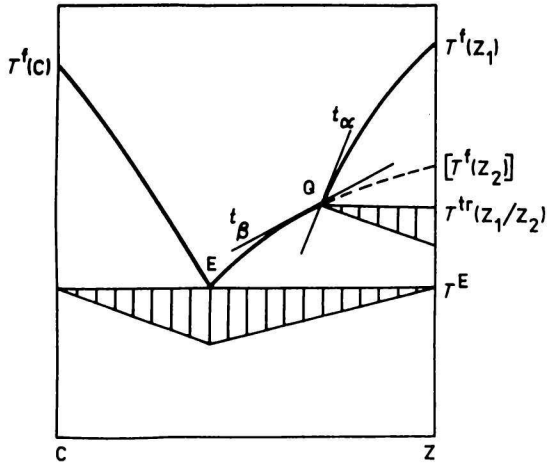
Fig. 2. Phase diagram of the condensed system C—Z₁ (Z₂) having neither compounds nor solid solutions.

approximately holds

$$k^{St}(Z/C) \cdot x(Z/C) = k^{St}(Z/D) \cdot x(Z/D) = \text{const} \qquad (6)$$

The terms $x(Z/C)$ and $x(Z/D)$ in eqn (6) denote the composition coordinate (given in mole fractions) of the transition point Q in the systems C—Z and D—Z, respectively [5].

It should be remarked that the phase diagrams presented in Figs. 1 and 2 have only schematic and qualitative character. *E.g.* the liquidus of component A or C is drawn as concave with respect to the composition axis. However, it can be proved that the concave or convex character of liquidus curve depends on the mutual relation of the quantities $\Delta H^{f}(i)$, $T^{f}(i)$, and $k^{St}(Z/i)$; $i = $ A or C [6]. Therefore the liquidus of the component i could be also convex with respect to the composition axis. This circumstances is not important in this case.

2. Systems with incongruently melting compound

For the systems of this type we can choose three characteristic cases of mutual arrangement of the temperatures of eutectic and peritectic reactions and temperatures of two modification transitions of the substances Z or B.

a) The case when $T(E) < T(P) < T^{tr}$

The phase diagram corresponding to this case is plotted in Fig. 3. For the slope of tangent $k^{0}(1/A)$ at the point $T^{f}(A)$ the relation (2) holds. The composition
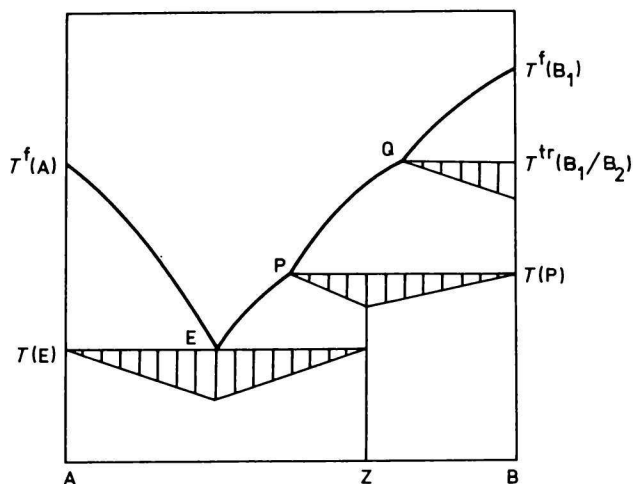
Fig. 3. Phase diagram of the condensed system A—B_1 (B_2) without solid solutions in which an incongruently melting compound Z is formed; $T(P) < T^{tr}(B_1/B_2)$.

coordinates of the liquidus curve l/A are to be transformed from the system A—B into the partial system A—Z.

The course of liquidus at the eutectic point E is governed by eqns (*3*) and (*4*), respectively. Also in this case a transformation of composition coordinates from the system A—B into the system A—Z is to be done.

In the peritectic point P the course of liquidus curves is given by the CTC IV [1] according to which

$$\Delta \bar{H}^{l/0, s}(Z) \cdot k(l/Z) = \Delta \bar{H}^{l/0, s}(B_2) \cdot k(l/B_2) \tag{7}$$

The quantities $\Delta \bar{H}^{l/0, s}(i)$ have the same meaning as in eqn (*3*). In the systems which are close to ideality and when the difference $T^f(B_1) - T(P)$ does not exceed 100 K, the quantities $\Delta \bar{H}^{l/0, s}(i)$ may be replaced by $\Delta H^f(Z)$ which is the formal enthalpy of fusion of Z; $\Delta H^f(B_2) = \Delta H^f(B_1) + \Delta H^{tr}(B_1/B_2)$. When applying the relationship (*7*) it is necessary to transform the composition coordinates from the system A—B into the system A—Z.

The course of liquidus curves in the transition point Q is governed by the CTC III. The corresponding relation holds in this case for the system A—B but not for the system A—Z.

b) The case when $T(E) < T^{tr} < T(P)$

The phase diagram corresponding to this case is plotted in Fig. 4. For the points $T^f(A)$, E, Q, and P the CTC I—IV can be applied similarly as in the former case.
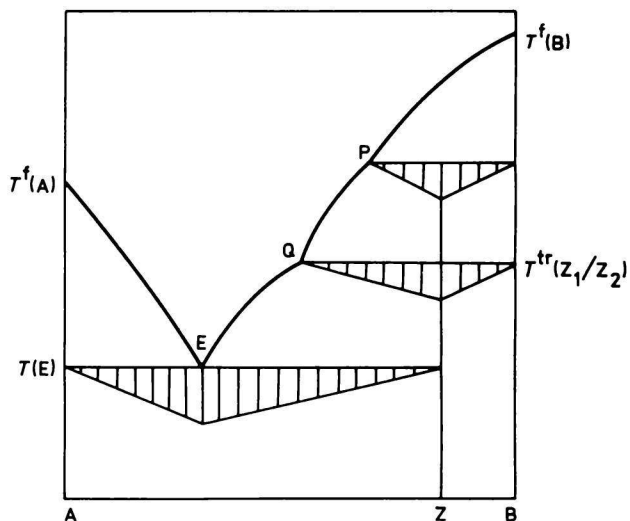
Fig. 4. Phase diagram of the condensed system A—B without solid solutions in which an incongruently melting compound Z is formed. This compound exists in two polymorphic modifications. It holds
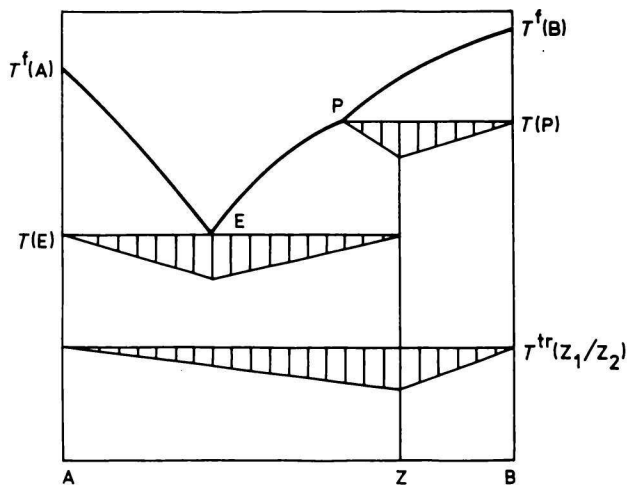$$T(E) < T^{tr}(Z_1/Z_2) < T(P).$$

Fig. 5. Phase diagram of the condensed system A—B without solid solutions in which an incongruently melting compound Z is formed. This compound exists in two polymorphic modifications. It holds
$$T^{tr}(Z_1/Z_2) < T(E) < T(P).$$

However, it is necessary to perform in all cases the transformation from the system A—B into the system A—Z.

c) The case when $T^{tr} < T(E) < T(P)$

The corresponding phase diagram is plotted in Fig. 5. For the points $T^f(A)$, E, and P the same criteria are valid as in the preceding cases. It is also necessary to transform the coordinates from the system A—B into the system A—Z.

The course of liquidus curve in the vicinity of $T^f(B)$ is in all last three cases determined by the CTC I. This rule holds in coordinates A—B.

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