Thermodynamics of phase equilibria in the systems with polymorphic transitions V. Systems in which continuous liquid and continuous solid solutions coexist and which contain complex compounds in the subsolidus region

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Thermodynamic analysis of three characteristic cases of phase equilibria in the systems of given type was carried out. The following cases are discussed: *1.* there is an explicit maximum (a distectoid point) on the curve of monovariant equilibrium of complex compound; *2.* this maximum exists only as an implicit one; *3.* the complex compound has not its own curve of monovariant phase equilibrium.

Rules which determine the values of slopes of tangents in remarkable points of the curves of monovariant equilibrium in these phase diagrams are derived.

Был осуществлен термодинамический анализ трех характеристических случаев фазового равновесия в системах данного типа. Обсуждаются следующие случаи: *1.* имеется явный максимум (дистектоидная точка) на кривой моновариантного равновесия комплексного соединения; *2.* этот максимум существует только в скрытом виде; *3.* комплексное соединение не имеет собственной кривой моновариантного фазового равновесия.

Были формулированы правила, определяющие значения наклонов касательных в характеристических точках кривых моновариантного равновесия на этих фазовых диаграммах.

We shall deal with three characteristic cases of formation of a complex compound in the subsolidus region.

1. The complex compound $Z=A_pB_q$ has its own curve of monovariant phase equilibrium and there is an explicit maximum on this curve

If no solid solutions are formed on the basis of substances A, Z or B we obtain the phase diagram which is illustrated in Fig. 1.

Let temperature of the pure compound Z be lower than $T(\delta)$. When we add heat to this compound, then a reaction takes place at the point δ (we shall call this point a distectoid one) which can be written as

$$Z_2^{0,\,s} \quad \rightarrow \quad Z_1 \qquad \text{(in solid solution)} \tag{1}$$

It is therefore a case of polymorphic transition. The molar enthalpy corresponding to the reaction (*1*) will be denoted as $\Delta H^{tr}(Z_1/Z_2)$. From the shape of the curve (ε_1, δ, ε_2) we can deduce that the compound thermally partially dissociates according to the scheme

$$(1-b_0)Z_1^{0,\,s} \quad \rightleftarrows \quad (p\cdot b_0)\bar{A}_1^s + (q\cdot b_0)\bar{B}_1^s \tag{2}$$

where b_0 is the degree of thermal dissociation of pure compound Z.

All three substances, *i.e.* A, B, and Z form one continuous solid solution. If this solution is not ideal another heat effect is connected with reaction (*2*). This effect equals the molar enthalpy of mixing ΔH_{mix}.

The original system A—B can be divided in the subsolidus region into two subsystems A—Z_2 and Z_2—B. In each of these subsystems there is a simple eutectoid point ε. In the point ε_1 we observe the reaction

$$(\bar{A}_1^s + \bar{B}_1^s) \quad \rightleftarrows \quad A_2^{0,\,s} + Z_2^{0,\,s} \tag{3}$$

and in the point ε_2 the reaction

$$(\bar{A}_1^s + \bar{B}_1^s) \quad \rightleftarrows \quad Z_2^{0,\,s} + B_2^{0,\,s} \tag{4}$$

It is possible to make a subsolidus cryoscopy in the system A—B, *viz.* on the basis of components A and B. However, it is to be taken into account that

$$k^{St}(Z/A) = 1 + (q-1)\cdot b_\infty; \quad k^{St}(Z/B) = 1 + (p-1)\cdot b_\infty$$

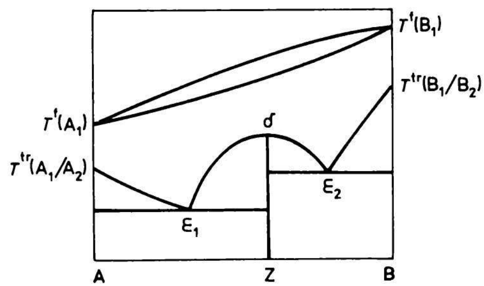

Fig. 1. Phase diagram of the condensed system $A_1(A_2)$—$B_1(B_2)$ having continuous solid solutions with respect to equilibrium "solidus—liquidus" and a complex compound with explicit maximum in the subsolidus region. This compound is in equilibrium with pure low temperature polymorphic modifications of components A and B.

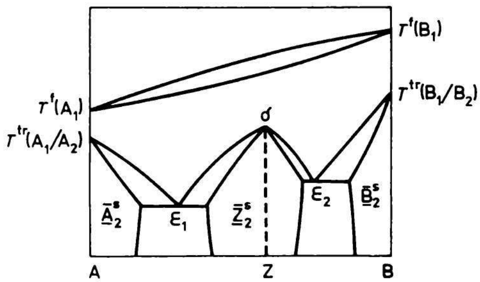

Fig. 2. Phase diagram of the condensed system $A_1(A_2)$—$B_1(B_2)$. High temperature modifications of components form continuous solid solutions. In the subsolidus region a complex compound with explicit maximum and limiting solid solutions on the basis of substances $\bar{A}_2^s$, $\bar{Z}_2^s$, and $\bar{B}_2^s$ are formed.

In this system A—B a classical cryoscopy cannot be done on the basis of the complex compound Z.

For the points $T^{tr}(A_1/A_2)$, $T^{tr}(B_1/B_2)$ the modified CTC I is valid. Similarly for points ε_1 and ε_2 the modified CTC II can be applied.

From the course of the curve of monovariant phase equilibrium (ε_1, δ, ε_2) of compounds Z one can determine the degree of thermal dissociation b_0 of pure compound Z in a similar way as in the case of "solidus—liquidus" equilibrium.

If in the subsolidus region limiting solid solutions are formed on the basis of all present substances we get the case which is illustrated in Fig. 2. The following equilibrium is established at the eutectoid points ε_1, ε_2

$$(\bar{A}_1^s + \bar{B}_1^s) \rightleftarrows \bar{A}_2^s + \bar{Z}_2^s \tag{5}$$

$$(\bar{A}_1^s + \bar{B}_1^s) \rightleftarrows \bar{Z}_2^s + \bar{B}_2^s \tag{6}$$

For the slopes of tangents to the curves of monovariant equilibrium at the points ε_1, ε_2 the modified Hagège relationship [1] can be applied (see also [2]).

The phase diagram presented in Fig. 1 is to be distinguished from that shown in Fig. 3. In the latter case there is splitting of the continuous solid solution into two limiting solid solutions which coexist in equilibrium. This subsolidus process starts at certain temperature and it goes according to the scheme

$$(\bar{A}^s + \bar{B}^s) \rightleftarrows (\bar{A}^s + \bar{B}^s) \tag{7}$$

If, for example, the component B forms two polymorphic modifications we obtain the phase diagram which is illustrated in Fig. 4. In this case the following equilibrium takes place at eutectoid point

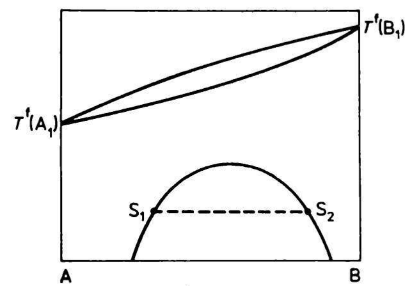

Fig. 3. Phase diagram of the condensed system A—B with continuous solid solutions with respect to "solidus—liquidus" equilibrium. At lower temperatures these solutions split into two solid solutions $\bar{A}^s$ and $\bar{B}^s$ with limiting miscibility.

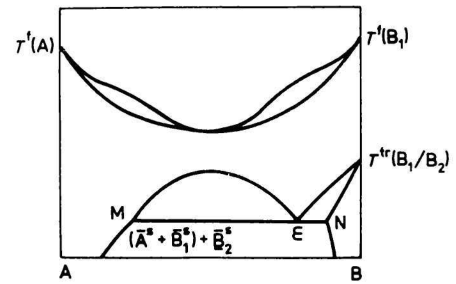

Fig. 4. Phase diagram of the condensed system A—$B_1(B_2)$ with continuous solid solutions with respect to "solidus—liquidus" equilibrium. In the subsolidus region they split at the eutectoid point into two limiting solid solutions formed on the basis of $\bar{A}^s$ and $\bar{B}^s$.

$$(\bar{A}_1^s+\bar{B}_1^s)[\varepsilon] \rightleftarrows (\bar{A}_1^s+\bar{B}_1^s)[M]+\underline{B}_2^s(N) \quad (8)$$

E.g. phase diagram of the system $NaNO_3(=A)$—$KNO_2(=B)$ (it has been experimentally determined by Jänecke [3]) is of the type presented in Fig. 4.

2. The complex compound Z has its own curve of monovariant phase equilibrium and there is an implicit maximum on this curve

The phase diagram of this type is illustrated in Fig. 5. It follows that solid solution coexists along the curve $[T^{tr}(B_1/B_2), \pi]$ with pure solid low temperature modification of substance B. At the temperature of peritectoid point $T(\pi)$ the following reaction occurs

$$(\bar{A}_1^s+\bar{B}_1^s)+B_2^{0,s} \rightleftarrows Z_2^{0,s} \quad (9)$$

Along the curve of monovariant equilibrium (π, ε) solid solution coexists with the modification $Z_2^{0,s}$. In this solid solution also the substance Z is present, *viz.* as modification Z_1. The formal molar quantity $\Delta H^f(Z)$ which is used for characterization of incongruent melting of complex compounds in the case of "solidus—liquidus" equilibrium is replaced in subsolidus region by the molar quantity $\Delta H^{tr}(Z_1/Z_2)$ which is connected with the reaction $Z_2^{0,s} \rightarrow Z_1^{0,s}$.

At the points $T^{tr}(A_1/A_2)$ and $T^{tr}(B_1/B_2)$ a modified CTC I can be applied. At the point π a modified CTC IV holds

$$[\Delta H^{tr}(Z_1/Z_2)+\Delta H_{mix}(\bar{Z}_1^s/Z_2^{0,s})]\cdot k^s(Z_1)=\Delta H^{tr}(B_1/B_2)\cdot k^s(B_1) \quad (10)$$

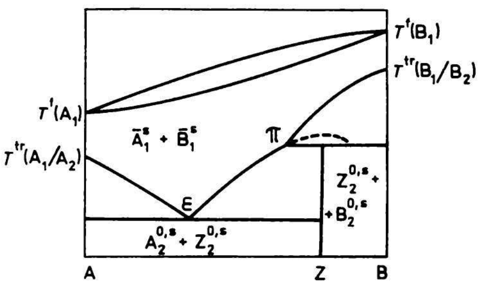

Fig. 5. Phase diagram of the condensed system $A_1(A_2)$—$B_1(B_2)$ with continuous solid solutions with respect to "solidus—liquidus" equilibrium. A complex compound with implicit maximum is formed in the subsolidus region. It coexists in equilibrium with pure low temperature polymorphic modifications of components A and B.

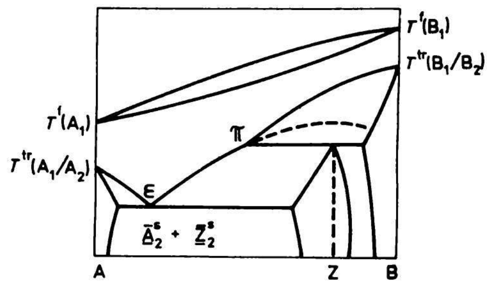

Fig. 6. Phase diagram of the condensed system $A_1(A_2)$—$B_1(B_2)$ with continuous solid solutions with respect to "solidus—liquidus" equilibrium. A complex compound with implicit maximum exists in the subsolidus region. Also limiting solid solutions on the basis of substances $\bar{A}_2^s$, $\bar{Z}_2^s$, and $\bar{B}_2^s$ are formed.

At the eutectoid point ε the modified CTC II can be applied

$$x_A \cdot [\Delta H^{tr}(A_1/A_2) + \Delta H_{mix}(\bar{A}_1^s/A_2^{0,s})] \cdot k^s(A_1) =$$
$$= x_Z \cdot [\Delta H^{tr}(Z_1/Z_2) + \Delta H_{mix}(\bar{Z}_1^s/Z_2^{0,s})] \cdot k^s(Z_1) \qquad (11)$$

When we apply the criteria of thermodynamic consistency to the curves at points $T^{tr}(A_1/A_2)$, ε, and π it is necessary to make a transformation of composition coordinates from the system A—B into the system A—Z.

If in the subsolidus region limiting solid solutions are formed on the basis of all present substances we get the phase diagram which is illustrated in Fig. 6.

Equilibrium which exists in the eutectoid point ε can be described by equation which is similar to eqn (*5*). For calculation of the slope of tangents to the curves at point ε the modified CTC II can be used [2]. It should be pointed out that composition of the point ε must be given in coordinates of the system A—Z.

3. *The complex compound Z has not its own curve of monovariant phase equilibrium*

Two typical cases of this class of phase diagrams are illustrated in Figs. 7 and 8. In the two former cases the complex compound Z coexisted with one "continuous" solid solution and thus the degrees of freedom equaled one. Therefore the equilibrium coexistence was fulfilled along a curve. In the present case there coexist

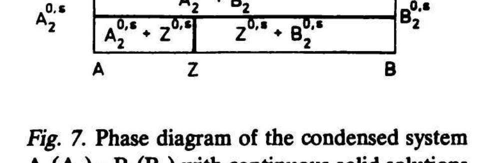

Fig. 7. Phase diagram of the condensed system $A_1(A_2)$—$B_1(B_2)$ with continuous solid solutions with respect to "solidus—liquidus" equilibrium. Low temperature polymorphic modifications of both components are completely immiscible. At temperature lower than is the temperature of the simple eutectoid point a complex compound is formed. It coexists with pure modifications $A_2^{0,s}$ and $B_2^{0,s}$.

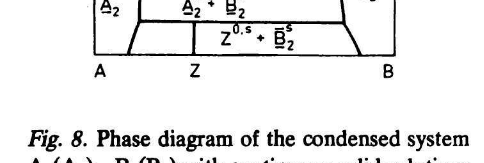

Fig. 8. Phase diagram of the condensed system $A_1(A_2)$—$B_1(B_2)$ with continuous solid solutions with respect to "solidus—liquidus" equilibrium. Low temperature polymorphic modifications of both components are partially miscible. At temperature lower than is the temperature of eutectoid point a complex compound is formed which coexists in equilibrium with limiting solid solutions $\bar{A}^s$ and $\bar{B}^s$.

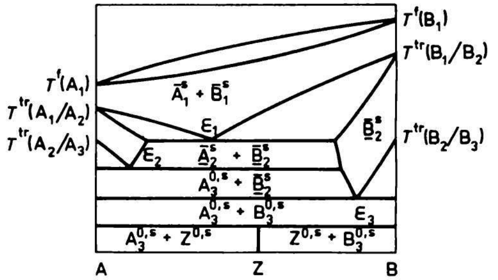

Fig. 9. Phase diagram of the condensed system $A_1(A_2, A_3)$—$B_1(B_2, B_3)$ with continuous solid solutions with respect to "solidus—liquidus" equilibrium. Three eutectoid points exist in the subsolidus region. At temperature $T < T(\varepsilon_3)$ a complex compound is formed. It coexists in equilibrium with pure modifications $A_3^{0,s}$ and $B_3^{0,s}$.

at temperature T(Z) the phases $A_2^{0,s}$, $Z^{0,s}$, and $B_2^{0,s}$ or phases $\bar{A}_2^s$, $Z^{0,s}$, and $\bar{B}_2^s$ and, therefore, the system is nonvariant.

It is known that in the case of systems formed by molten salts there is a general tendency to decrease of mutual solubility in solid state. This tendency is illustrated on a typical example in Fig. 9.

References

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