Criteria of thermodynamic consistency. I.
Systems having no solid solutions*

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General laws describing the course of liquidus curves in the binary systems having no solid solutions have been formulated or derived. They are called the criteria of thermodynamic consistency. It has been proved that the relations are generally valid without respect to functional relation between the activity and the concentration of the component in liquid phase. The criteria can be used successfully for the verification of principal correctness of the course of a liquidus curve.

For the equilibrium "solidus—liquidus" the classic thermodynamics yields at $P = $ = const relation [1]

$$\ln a_A = \Delta H_A^f \left[1/T_A^f - 1/T_A \right] R^{-1} + \frac{1}{R} \int_{T_A}^{T_A^f} \left[1/T_A^2 \cdot \int_{T_A}^{T_A^f} \Delta C_P^{l/s} \, dT \right] dT, \qquad (1)$$

where a_A is the activity of component A in liquid solution which coexists in equilibrium with the pure solid component A,

ΔH_A^f is the change in enthalpy accompanying the process $A_s \rightarrow A_1$ at T_A^f,

T_A^f is the temperature of fusion of the pure component A,

T_A is the temperature of primary crystallization of the pure component A in liquid phase in which the activity of component A equals a_A,

$\Delta C_P^{l/s}$ is the change in the molar heat capacity for the process $A_s \rightarrow A_1$,

R is the gas constant.

If we intend to calculate the course of a liquidus curve in coordinates $x_A - T_A$, where x_A is the mole fraction of component A in the system A—B, we should know the functional dependence $a_A = f(x_A)$. This relation can be empirical, semiempirical, or rational, obtained by a mathematical treatment of physical properties of the chosen model of the liquid phase.

However, it can be proved that there are such regions in the diagrams of liquidus where the course of liquidus curves is strictly determined by certain thermodynamic relations which are completely independent of the chosen model or of the dependence $a_A = f(x_A)$. These universal rules will be called *the criteria of thermodynamic consistency* for the course of liquidus curves.

1st criterion:

For the course of the liquidus curve of component A in a simple eutectic binary system A—B it holds

$$\lim_{x_A \to 1} \frac{dT_A}{dx_A} = \mathrm{tg}\ \alpha_A = R(T_A^f)^2 \cdot k_{B/A}^{St}/\Delta H_A^f, \tag{2}$$

where α_A is the angle between tangent to the liquidus curve of component A for $x_A \to 1$ and the isotherm (Fig. 1),

$k_{B/A}^{St}$ is the Stortenbeker correction factor equal to the number of gram-moles of new particles in the system (formed by a great excess of substance A) which appear as the result of the addition of 1 mole of substance B.

The necessity to introduce the correction factor follows from the considerations published by *Stortenbeker* [2]. That is why we will call the correction factor by his name. Relation (2) can be rationally derived on the basis of the *Temkin* model of ideal ionic systems [3—5] or on the base of the universal relation for the functional dependence $a = f(x)$ [6].

If the experimentally found course of the liquidus in the given system does not obey this criterion it may be supposed that the measurements are wrong [7, 8]. Also the model from which this criterion does not follow for $x_A \to 1$ seems to be incorrect.

2nd criterion:

For the course of liquidus curves near the eutectic point E in a simple binary system A—B it holds

$$x_A^E \cdot \Delta \overline{H}_{A(E)}^{l/s} \cdot k_A^E = x_B^E \cdot \Delta \overline{H}_{B(E)}^{l/s} \cdot k_B^E, \tag{3}$$

where x_A^E, x_B^E are the coordinates of the eutectic point E in the given system,

$\Delta \overline{H}_{A(E)}^{l/s}$, $\Delta \overline{H}_{B(E)}^{l/s}$ are the partial molar changes in the enthalpy of the processes $A_s \to \overline{A}_l$ and $B_s \to \overline{B}_l$ at the composition and temperature of the point E,

k_A^E, k_B^E are the slopes of tangents to the liquidus curves A or B at the point E (Fig. 2). Apparently $k_A^E = \mathrm{tg}\ \alpha$, $k_B^E = \mathrm{tg}\ \beta$.

Relation (3) has been derived by *Dodé* and *Hagège* [9]. Later, using this relation, the equation for the determination of changes in partial molar enthalpies of mixing at the point E has been proposed [10]. An application of eqn (3) is in papers [8, 11].
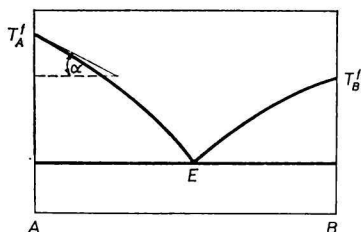

Fig. 1. The course of the liquidus curve at the melting point of the pure component A according to the 1st criterion.
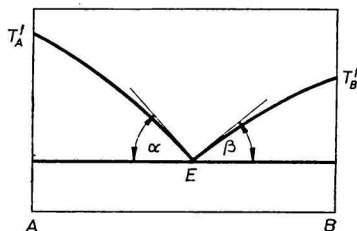

Fig. 2. The course of the liquidus curves of components A and B near the eutectic point E according to the 2nd criterion.
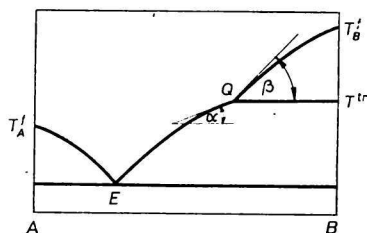
Fig. 3. The course of the liquidus curves of component B near the point Q according to the 3rd criterion.
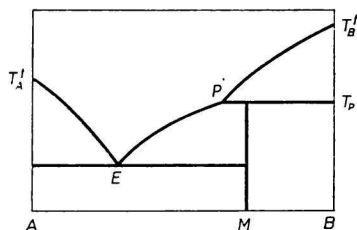
Fig. 4. Phase diagram of the binary system A—B having an incongruently melting compound M.

The relations forming the content of the 1st and the 2nd criterion of thermodynamic consistency are therefore known. It seems however that their fundamental importance for the verification of the principal correctness of the course of liquidus curves has not yet been fully comprehended and therefore they have not been used in this sense as yet.

3rd criterion:

Let us consider a binary system A—B in which a polymorphic change *e.g.* $B_\alpha \rightleftarrows B_\beta$ appears at the temperature $T_{\beta/\alpha}^{tr}$. Let $T_E < T_{\beta/\alpha}^{tr} < T_\beta^f$. The low-temperature modification of component B will be denoted B_α, the high-temperature modification B_β. Then for the course of the liquidus curve of component B in the vicinity of nonvariant point Q (Fig. 3) it holds

$$\Delta \bar{H}_{B_\alpha (Q)}^{l/s} \cdot k_\alpha^Q = \Delta \bar{H}_{B_\beta (Q)}^{l/s} \cdot k_\beta^Q, \tag{4}$$

where $\Delta \bar{H}_{B_\alpha (Q)}^{l/s}$, $\Delta \bar{H}_{B_\beta (Q)}^{l/s}$ are the partial molar changes in enthalpy for the processes

$$B_\alpha^s \rightarrow \bar{B}_{(Q)}^l, \quad B_\beta^s \rightarrow \bar{B}_{(Q)}^l,$$
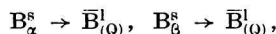
k_α^Q, k_β^Q are the slopes of tangents to liquidus curves of component B at the point Q.

It holds that $k_\alpha^Q = \text{tg } \alpha$, $k_\beta^Q = \text{tg } \beta$.

Derivation of eqn (*4*):

From the condition of thermodynamic equilibrium for the reaction $B_\alpha^s \rightleftarrows \bar{B}^l$ it follows

$$d(G_{B_\alpha}^{0,s}/T)_P = d(\bar{G}_{B_\alpha}^l/T)_P, \tag{5}$$

$$\frac{\partial}{\partial T}(G_{B_\alpha}^{0,s}/T)\, dT = \frac{\partial}{\partial T}(\bar{G}_{B_\alpha}^l/T)_x\, dT + \frac{\partial}{\partial x}(\bar{G}_{B_\alpha}^l/T)_T\, dx,$$

$$-\frac{H_{B_\alpha}^{0,s}}{T^2}\, dT = -\frac{\bar{H}_{B_\alpha}^l}{T^2}\, dT + \frac{\partial}{\partial x}\left(\frac{G_{B_\alpha}^{0,l} + RT \ln a_{B_\alpha}^l}{T}\right)_T\, dx.$$

As $G_{B_\alpha}^{0,l}/T$ does not depend on x, it holds after rearrangement (see [10])

$$\Delta \bar{H}_{B_\alpha}^{l/s}\left(\frac{dT_{B_\alpha}}{dx_{B_\alpha}}\right)_{eq} = RT^2\left(\frac{\partial \ln a_{B_\alpha}^l}{\partial x_{B_\alpha}}\right)_{P,T} \tag{6a}$$

and similarly for the equilibrium $B_\beta^s \rightleftarrows \bar{B}^l$ it can be written

$$\Delta \bar{H}_{B_\beta}^{l/s}\left(\frac{dT_{B_\beta}}{dx_{B_\beta}}\right)_{eq} = RT^2\left(\frac{\partial \ln a_{B_\beta}^l}{\partial x_{B_\beta}}\right)_{P,T}. \tag{6b}$$
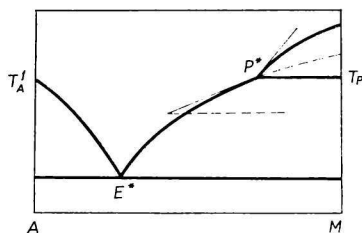
Fig. 5. The course of the liquidus curve of compound M and substance B near the peritectic point P* in the system A — M according to the 4th criterion.

At the point Q, $x_{B_\alpha} = x_{B_\beta}$, and therefore $dx_{B_\alpha} = dx_{B_\beta}$; $T_Q = T^{tr}$.

$$\left(\frac{dT_{B_\alpha}}{dx_{B_\alpha}}\right)_{eq} = k_\alpha^Q; \qquad \left(\frac{dT_{B_\beta}}{dx_{B_\beta}}\right)_{eq} = k_\beta^Q.$$

Comparing eqns (*6a*) and (*6b*) we obtain relation (*4*). Dividing eqn (*4*) by $T^{tr} \neq 0$ gives

$$\Delta \bar{S}_{B_\alpha (Q)}^{l/s} \cdot k_\alpha^Q = \Delta \bar{S}_{B_\beta (Q)}^{l/s} \cdot k_\beta^Q. \tag{7}$$

4th criterion:

Let us consider a binary system A — B having an incongruently melting compound M (Fig. 4). Let us make a transformation of concentration coordinates in such a way that the system A — B will be divided into two independent systems A — M and M — B (Fig. 5). It is evident that the system A — M is a topological analogue of the system A — B (Fig. 3). Using the similar way as in the case of the 3rd criterion it can be proved that for the course of liquidus curves of compound M and component B near the point P* it holds

$$\Delta \bar{H}_{M (P^*)}^{l/s} \cdot k_M^{P^*} = \Delta \bar{H}_{B (P^*)}^{l/s} \cdot k_B^{P^*}. \tag{8}$$

The symbols in eqn (*8*) have the same meaning as in the previous relations. The asterisks in eqn (*8*) denote that all the parameters are related to the systems A — M (Fig. 5). This system has been constructed from the system A — B (Fig. 4) by the transformation of concentration coordinates and therefore in the system A — M it holds that $x_A + x_M = 1$.

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Translated by P. Fellner