

COMMON EXTREME ON THE LIQUIDUS AND SOLIDUS CURVES  
IN SYSTEMS WITH UNLIMITED LIQUID  
AND SOLID SOLUTIONS

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The title problem is solved both with the characteristic equation and without the characteristic equation. Necessary conditions are derived for the existence of the common extreme on the liquidus and solidus curves. An equation for the extreme is arranged which enables one to calculate the composition at the extreme. A formula for calculating the corresponding temperature at the extreme is presented. A so-called principle of monotonicity is introduced which gives the sufficient condition for monotonic course of the liquidus and solidus curves. The developed theory is demonstrated on an example of a solution with common ion where the liquidus and solidus lines have a common minimum and the universal functional relationship holds between activity and composition. A concrete case of the course of the liquidus and solidus curves in the  $N_qA_3$ — $N_qB_3$  system is expressed graphically.

This work follows our previous paper<sup>1</sup>. For the course of liquidus and solidus lines we have derived the system of relations which we further use to derive the equation of extreme:

$$dT/dx = -(\partial F/\partial x)/(\partial F/\partial T), \quad (1)$$

$$\partial F/\partial x_1^1 = Q(d\psi_2/dx_1^s)(\partial x_1^s/\partial x_1^1) - d\varphi_2/dx_1^1, \quad (2)$$

$$x_1^s = \phi(M, x_1^1), \quad (3)$$

$$M = \varphi_1(x_1^1)/\psi_1(x_1^s) = \exp \left[ \frac{\Delta H_1^f}{R} \left( \frac{1}{T_1^f} - \frac{1}{T} \right) \right], \quad (4)$$

$$Q = \varphi_2(x_1^1)/\psi_2(x_1^s) = \exp \left[ \frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T} \right) \right], \quad (5)$$

where  $F$  is the symbol for the characteristic equation of the liquidus line,  $T$  is absolute

temperature,  $x$  mole fraction,  $x_1^l$ ,  $x_1^s$  are mole fractions of the first component in the liquid and solid states, respectively. The symbols  $\varphi_1$ ,  $\varphi_2$ ,  $\psi_1$ ,  $\psi_2$  denote the functional relations between activity and composition of both components in liquidus and solidus.  $\Delta H_i^f$  is the change of molar enthalpy of pure  $i$ -th component at melting temperature  $T_i^f$  at the phase solidus-liquidus transition.

The sufficient condition for the existence of an extreme on the curve of liquidus or solidus inside the (0·1) interval is the inequality

$$\text{sign} \left[ \lim_{T \rightarrow T_1^f} (dT/dx) \right] \neq \text{sign} \left[ \lim_{T \rightarrow T_2^f} (dT/dx) \right].$$

### The Case with Characteristic Equation of the Liquidus Curve

If there exists a common extreme on the liquidus and solidus curves the following requirements must be fulfilled:

a) at the extreme holds  $x_1^l = x_1^s = x_{ex}$ , b)  $(\partial F/\partial x)_{x=x_{ex}} = 0$  on the assumption that  $(\partial F/\partial T)_{x=x_{ex}} \neq 0$  (see Eqs (1) and (2)), c)  $F(x_{ex}, T_{ex}) = 0$ , where  $F(x, T) = 0$  is the characteristic equation for the liquidus line.

When introducing the denotation:

$$\begin{aligned} \left[ \frac{d\varphi_2(x_1^l)}{dx_1^l} \right]_{x_1^l=x_{ex}} &= \varphi_2'(x_{ex}), \\ \left[ \frac{d\psi_2(x_1^s)}{dx_1^s} \right]_{x_1^s=x_{ex}} &= \psi_2'(x_{ex}), \\ \left[ \frac{\partial x_1^s}{\partial x_1^l} \right]_{x_1^l=x_{ex}} &= \left[ \frac{\partial \phi}{\partial x_1^l} \right]_{x_1^l=x_{ex}} = \phi'(x_{ex}), \end{aligned}$$

we get the relation (6) for the value of the function  $Q$  at the extreme

$$Q_{ex} = \frac{\varphi_2'(x_{ex})}{\psi_2'(x_{ex})} \cdot \frac{1}{\phi'(x_{ex})}. \quad (6)$$

The relation (6) comprises the requirements a) and b). If the requirement c) is to be simultaneously satisfied, too, the relation (6) must be identical with the relation (5) in which, however, we must write  $x_1^l = x_1^s = x_{ex}$ .

Thus, we get the identity

$$\frac{\varphi_2'(x_{ex})}{\psi_2'(x_{ex})} \cdot \frac{1}{\phi'(x_{ex})} \equiv \frac{\varphi_2(x_{ex})}{\psi_2(x_{ex})}, \quad (7)$$

which we call the checking identity. If it is not possible to fulfil the checking identity for some form of functional dependence  $a = \varphi(x)$  the respective functional dependence is not suitable for expressing the equation of the liquidus and solidus lines with extreme. With respect to Eq. (3) there are two unknowns in Eq. (6), viz. the composition at the extreme  $x_{\text{ex}}$  and the temperature at the extreme  $T_{\text{ex}}$ . As the second equation we shall use the relation (4) with  $T = T_{\text{ex}}$ :

$$M_{\text{ex}} = \frac{\varphi_1(x_{\text{ex}})}{\psi_1(x_{\text{ex}})} = \exp\left(\frac{\Delta H_1^f}{R} \left(\frac{1}{T_1^f} - \frac{1}{T_{\text{ex}}}\right)\right). \quad (8)$$

With respect to the identity (7) and Eq. (8), we can take logarithm of Eq. (6):

$$\frac{\Delta H_2^f}{R} \left(\frac{1}{T_2^f} - \frac{1}{T_{\text{ex}}}\right) = \ln \frac{\varphi_2(x_{\text{ex}})}{\psi_2(x_{\text{ex}})},$$

$$\frac{\Delta H_1^f}{R} \left(\frac{1}{T_1^f} - \frac{1}{T_{\text{ex}}}\right) = \ln \frac{\varphi_1(x_{\text{ex}})}{\psi_1(x_{\text{ex}})}.$$

By eliminating  $T_{\text{ex}}$  from them and after rearranging we obtain the equation

$$\frac{\varphi_2(x)}{\psi_2(x)} \cdot \left(\frac{\varphi_1(x)}{\psi_1(x)}\right)^{-\Delta H_2^f/\Delta H_1^f} = Q_0, \quad (9)$$

which can be called the equation of extreme, where

$$Q_0 = \exp\left(\frac{\Delta H_2^f}{R} \left(\frac{1}{T_2^f} - \frac{1}{T_1^f}\right)\right).$$

The temperature at the extreme is then calculated from Eq. (8).

#### *The Case without Characteristic Equation of the Liquidus Curve*

In the foregoing paper<sup>1</sup> the relation (20) is presented for the tangent slope to the liquidus curve. Hence it follows for the extreme

$$Q_{\text{ex}} = \frac{\varphi_2'(x_{\text{ex}}) \cdot M(x_{\text{ex}}) \cdot \psi_1'(x_{\text{ex}})}{\varphi_1'(x_{\text{ex}}) \cdot \psi_2'(x_{\text{ex}})}.$$

The checking identity takes in this case the form

$$\frac{\varphi_2'(x_{\text{ex}}) \cdot \psi_1'(x_{\text{ex}}) \cdot \varphi_1(x_{\text{ex}})}{\varphi_1'(x_{\text{ex}}) \cdot \psi_2'(x_{\text{ex}}) \cdot \psi_1(x_{\text{ex}})} \equiv \frac{\varphi_2(x_{\text{ex}})}{\psi_2(x_{\text{ex}})} \quad (10)$$

On making use of a quite analogous procedure to the case with the characteristic equation for the liquidus line we obtain the system of equations:

$$\frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T_{\text{ex}}} \right) = \ln \frac{\varphi_2(x_{\text{ex}})}{\psi_2(x_{\text{ex}})},$$

$$\frac{\Delta H_1^f}{R} \left( \frac{1}{T_1^f} - \frac{1}{T_{\text{ex}}} \right) = \ln \frac{\varphi_1(x_{\text{ex}})}{\psi_1(x_{\text{ex}})}.$$

By eliminating  $T_{\text{ex}}$  and rearranging we again get to the same form of the equation of extreme (Eq. (9)). The temperature at the extreme is then calculated from the relation (8).

#### *Existence Criterion of Extreme*

An important conclusion follows from our present analysis for the existence of extreme on the liquidus and solidus curves. In the case of a minimum on the liquidus and solidus lines it holds  $T_{\text{ex}} < \min(T_1^f, T_2^f)$  and with respect to the defining equations of the functions  $M$  and  $Q$  (Eqs (4) and (5)) holds

$$M_{\text{ex}} < 1 \wedge Q_{\text{ex}} < 1. \quad (11)$$

Analogously in the case of a maximum on the liquidus and solidus curves  $T_{\text{ex}} > \max(T_1^f, T_2^f)$ , from which follows

$$M_{\text{ex}} > 1 \wedge Q_{\text{ex}} > 1. \quad (12)$$

The relations (11) and (12) together with the checking identity (7) enable one to decide directly, on the basis of the form of functional dependence between activity and composition, whether the given functional dependence allows the existence of the respective extreme. The relations (11) and (12) are therefore called the existence criterion of extreme.

#### *Principle of Monotonicity*

The existence criterion has, however, another important consequence which we call the principle of monotonicity. From the definitions of functions  $M$  and  $Q$  (Eqs (4)

and (5)) follows: If the same functional dependence between activity and composition holds both for the liquidus and for the solidus curves the value of  $M$  and  $Q$  functions at the common extreme of the liquidus and solidus curves is identically equal to unity,

$$M_{\text{ex}} = \frac{\varphi_1(x_{\text{ex}})}{\varphi_1(x_{\text{ex}})} \equiv 1, \quad Q_{\text{ex}} = \frac{\varphi_2(x_{\text{ex}})}{\varphi_2(x_{\text{ex}})} \equiv 1,$$

which excludes the existence of extreme within the interval  $\langle 0,1 \rangle$ . Thus, the principle of monotonicity states: If the functional dependence between activity and composition is identical both in the liquidus and solidus and when we assume the validity of the relations (4) and (5) the course of the curves can be only monotonous regardless of the form of the above-mentioned functional dependence.

The principle of monotonicity follows as well from the form of Eq. (9) for extreme. If the functional dependence between activity and composition is the same in the liquidus and solidus it follows from Eq. (9)

$$1 = Q_0 = \exp\left(\frac{\Delta H_2^f}{R} \left(\frac{1}{T_2^f} - \frac{1}{T_1^f}\right)\right),$$

which cannot be fulfilled for  $T_2^f \neq T_1^f$ .

*Example:* Let us consider a system with a common ion  $N_p A_q - N_r B_t$  for which a universal functional relation<sup>2</sup>  $a = x^k$  holds in liquidus, where  $k$  is the number of new particles brought with the second component into the solution. In solidus let the solution be classically ideal, i.e.  $a = x$ . The relations (3) introduced in the paper<sup>1</sup> are then:

$$\begin{aligned} a_1^l &= \varphi_1(x_1^l) = (x_1^l)^t & a_1^s &= \psi_1(x_1^s) = x_1^s, \\ a_2^l &= \varphi_2(x_1^l) = (1 - x_1^l)^q & a_2^s &= \psi_2(x_1^s) = 1 - x_1^s, \end{aligned}$$

where  $a_i^l, a_i^s$  are activities of the  $i$ -th component in liquidus and solidus, respectively. For the needed functional relations and derivatives we have

$$\begin{aligned} \varphi_2'(x_1^l) &= -q \cdot (1 - x_1^l)^{q-1}, \quad \psi_2'(x_1^s) = -1, \\ M &= \frac{(x_1^l)^t}{x_1^s}, \quad Q = \frac{(1 - x_1^l)^q}{(1 - x_1^s)}, \quad \phi(M, x_1^l) = \frac{1}{M} (x_1^l)^t, \\ \frac{\partial \phi}{\partial x_1^l} &= \frac{1}{M} t \cdot (x_1^l)^{t-1}, \quad \left(\frac{\partial \phi}{\partial x_1^l}\right)_{x=x_{\text{ex}}} = t. \end{aligned}$$

The checking identity (Eq. (7)) becomes

$$q \cdot (1 - x)^{q-1} \equiv t \cdot (1 - x)^{q-1} \Rightarrow q = t.$$

The existence criterion for minimum under the condition  $q = t$  is

$$x^{q-1} < 1 \wedge (1 - x)^{q-1} < 1.$$

If  $q = 1$  then  $x^{q-1} = (1 - x)^{q-1} = 1$  and consequently no extreme can occur. In this case the solution is classically ideal, *i.e.* in the liquidus as well as in the solidus the same functional dependence  $a = x$  holds. On the basis of the principle of monotonicity the course of the curves is then monotonous. When  $q > 1$  the existence criterion is fulfilled regarding the fact that, in the considered system, for the composition  $x$  always holds  $0 < x < 1$ .

Altogether we get this result: In case of binary systems with a common ion, when a universal functional relationship holds between activity and composition in liquidus and the solution is classically ideal in solidus, the minimum may occur if holds

$$q = t \wedge q > 1,$$

*i.e.* the solution is of the  $N_pA_q-N_rB_q$  type.

If a minimum is to be investigated the existence criterion takes the form

$$x^{q-1} > 1 \wedge (1 - x)^{q-1} > 1,$$

which, for  $q \geq 1$  and for  $0 < x < 1$ , cannot be fulfilled. Solution of the given type cannot consequently form a common maximum on the liquidus and solidus curves.

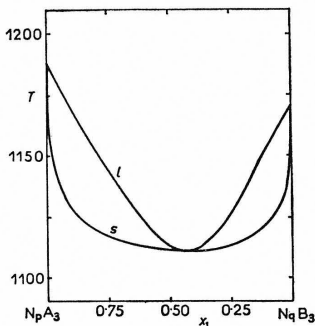


FIG. 1

Phase Diagram of a System with Common Ion

$N_pA_3-N_qB_3$ ,  $T/K$  Type

*l* Liquidus curve, *s* solidus curve.

The equation of the extreme is

$$(1 - x)^{q-1} \cdot x^{(1-q) \cdot \Delta H_2^f / \Delta H_1^f} = Q_0$$

when  $q > 1$ .

The phase diagram for a concrete case of a solution of this type for  $q = t = 3$  when choosing the values  $T_1^f = 1073$  K,  $T_2^f = 1043$  K,  $\Delta H_1^f = 88.6$  kJ.mol<sup>-1</sup>,  $\Delta H_2^f = 76.6$  kJ.mol<sup>-1</sup> was solved with a Siemens 4004 computer and is illustrated in Fig. 1.

#### REFERENCES

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