

## LIQUIDUS AND SOLIDUS LINES IN BINARY SYSTEMS WITH UNLIMITED LIQUID AND SOLID SOLUTIONS

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A thermodynamic and mathematical analysis was performed of liquidus and solidus lines in binary 2nd kind ionic systems with unlimited solubility in both the liquid and solid states. Limiting values of tangent slopes of liquidus and solidus lines at melting points of pure components were calculated. The analysis is supplemented by two examples.

In contrast to our earlier paper<sup>1</sup>, where we have performed a theoretical analysis of liquidus and solidus lines in binary NA–NB<sub>i</sub> ionic system with a common ion and displaying unlimited solubility in both the liquid and solid states, here we solve the problems in general.

The analysis of the course of liquidus and solidus lines refers again to binary ionic systems. However, we consider systems with a common ion and without a common ion, but with unlimited solubility in both the liquid and solid states. We assume that the systems form solutions of the 2nd kind, *i.e.* such solutions which generally satisfy the relation:  $\lim (da_i/dx_i) \neq 1$  [for  $x_i \rightarrow 1$ ] for  $i = 1, 2$ . Symbol  $a_i$  denotes the activity and  $x_i$  mole fraction of component  $i$ .

Our aim is to express analytically the functional dependences  $x_1^l = f_1(T)$ ,  $x_1^s = f_2(T)$ , where symbols  $x_1^l$  and  $x_1^s$  denote mole fractions of component 1 in liquidus and solidus, resp., and  $T$  is absolute temperature. Then we will derive limiting values of tangent slopes at melting points  $T_1^f$  and  $T_2^f$  of both pure components.

### *Derivation of Liquidus and Solidus Lines*

Let us consider a solid–liquid equilibrium. For this case the classical thermodynamics yields the fundamental relations, which have been derived in this journal<sup>2</sup> and in which the validity of the relation  $\Delta C_p^{l/s} \approx 0$  has been assumed

$$M(a_1^l, a_1^s) = \frac{a_1^l}{a_1^s} = \exp \left[ \frac{\Delta H_1^f}{R} \left( \frac{1}{T_1^f} - \frac{1}{T} \right) \right], \quad (1)$$

$$Q(a_2^1, a_2^s) = \frac{a_2^1}{a_2^s} = \exp \left[ \frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T} \right) \right]. \quad (2)$$

Here,  $\Delta C_p^{1/s}$  denotes the change in the molar heat capacity during the solidus–liquidus phase transition at constant pressure,  $\Delta H_i^f$  is the change in the molar enthalpy of pure component  $i$  at its melting temperature  $T_i^f$  during the solidus–liquidus phase transition.

To be able to pass from activity to composition expressed in mole fractions, we need to know the functional relation  $a = \varphi(x)$ . Generally, however, it is impossible. Therefore we usually replace it by relations which for the most part follow from different models. However, up to the present time no exhaustive analysis of possibilities has been performed how to employ these functional relations for solving the given problems.

The classical ideal case of  $a_i = x_i$  has been solved in this journal<sup>2</sup>. Generally, the activity is a function of composition and temperature, *i.e.*  $a = \varphi(x, T)$ . However, we are going to deal only with the solidus–liquidus equilibrium, where the activity depends only on composition, *i.e.*  $a = \varphi(x)$ . Therefore we assume the validity of the general functional relations in the form of

$$\begin{aligned} a_1^1 &= \varphi_1(x_1^1) & a_1^s &= \psi_1(x_1^s) \\ a_2^1 &= \Omega_1(x_2^1) = \Omega_1(1 - x_1^1) = \varphi_2(x_1^1) & a_2^s &= \Omega_2(x_2^s) = \Omega_2(1 - x_1^s) = \psi_2(x_1^s) \end{aligned} \quad (3)$$

in which we make use of the identities  $x_1^1 + x_2^1 = 1$ ,  $x_1^s + x_2^s = 1$ . Further we assume that functions (3) are on interval  $(0, 1)$  monotonous<sup>3,4</sup>, differentiable and possess right and left limits at the boundary points of this interval. These limits must satisfy the following boundary conditions:

$$\begin{aligned} \lim_{x_1^1 \rightarrow 0_+} \varphi_1(x_1^1) &= 0 & \lim_{x_1^s \rightarrow 0_+} \psi_1(x_1^s) &= 0 \\ \lim_{x_1^1 \rightarrow 1_-} \varphi_1(x_1^1) &= 1 & \lim_{x_1^s \rightarrow 1_-} \psi_1(x_1^s) &= 1 \\ \lim_{x_1^1 \rightarrow 0_+} \varphi_2(x_1^1) &= 1 & \lim_{x_1^s \rightarrow 0_+} \psi_2(x_1^s) &= 1 \\ \lim_{x_1^1 \rightarrow 1_-} \varphi_2(x_1^1) &= 0 & \lim_{x_1^s \rightarrow 1_-} \psi_2(x_1^s) &= 0 \end{aligned} \quad (4)$$

where symbol  $x_1^1 \rightarrow 0_+$  denotes the right limit and symbol  $x_1^1 \rightarrow 1_-$  the left limit. By inserting (3) into (1) and (2) we obtain the set of equations

$$M(x_1^1, x_1^s) = \frac{\varphi_1(x_1^1)}{\psi_1(x_1^s)} = \exp \left[ \frac{\Delta H_1^f}{R} \left( \frac{1}{T_1^f} - \frac{1}{T} \right) \right], \quad (5)$$

$$Q(x_1^l, x_1^s) = \frac{\varphi_2(x_1^l)}{\psi_2(x_1^s)} = \exp \left[ \frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T} \right) \right], \quad (6)$$

which express implicitly on interval  $(T_2^f, T_1^f)$  the required functions  $x_1^l = f_1(T)$ ,  $x_1^s = f_2(T)$  with the range of functional values of  $(0, 1)$ .

If functional relations (3) are monotonous and differentiable on the closed interval  $\langle 0, 1 \rangle$ , functions  $x_1^l = f_1(T)$  and  $x_1^s = f_2(T)$  are given implicitly by Eqs (5), (6) on the closed interval  $\langle T_1^f, T_2^f \rangle$ .

In the following we will distinguish the two cases: a) if  $x_1^s$  resp.  $x_1^l$  may be expressed explicitly from (5) or (6) as functions of  $M$ ,  $x_1^l$  resp.  $M$ ,  $x_1^s$ , it is then possible to construct the so-called characteristic equation for the liquidus resp. solidus line. This situation will be denoted as the case with the characteristic equation.

b) if, due to a complicated form of functional dependences (3), this explicit evaluation is impossible, we will denote it as the case without the characteristic equation.

#### Case with the Characteristic Equation

If  $x_1^s$  may be expressed explicitly from (5), we will introduce the notation

$$x_1^s = \Phi(M, x_1^l). \quad (7)$$

Simultaneously it holds

$$\lim_{T \rightarrow T_1^f} \Phi(M, x_1^l) = 1 \quad \lim_{T \rightarrow T_2^f} \Phi(M, x_1^l) = 0$$

By inserting (7) into (2) we obtain

$$Q = \frac{\varphi_2(x_1^l)}{\psi_2[\Phi(M, x_1^l)]}$$

and by performing the multiplication we get the equation

$$Q\psi_2[\Phi(M, x_1^l)] - \varphi_2(x_1^l) = 0 \equiv F(x, T) \quad (8)$$

which will be denoted as the characteristic equation.

Coefficients in this characteristic equation depend through functions  $M$  and  $Q$  on temperature  $T$  and on values of the enthalpy of fusion  $\Delta H_1^f$  and  $\Delta H_2^f$ . Besides that they also depend on values of the stoichiometric coefficients  $p$ ,  $q$ ,  $r$ ,  $t$ . Thus we obtain for each value of  $T \in (T_1^f, T_2^f)$  the equation with different coefficients. If relations (3) are rational functions of variables  $x_1^l$  and  $x_1^s$ , the characteristic equation is usually the algebraic equation and its order depends on values of the stoichiometric coefficients  $p$ ,  $q$ ,  $r$ ,  $t$ .

It is well-known<sup>5</sup> that every algebraic equation of the  $n$ -th order possesses  $n$  roots. If the characteristic equation is to be the equation of the liquidus line, it must have for each value of  $T \in (T_1^f, T_2^f)$  at least one root in the interval  $(0, 1)$ ; for this root, a continuous change in temperature  $T$  from  $T_2^f$  to  $T_1^f$  must correspond to a continuous change in composition from 0 to 1.

The unknown quantity in the characteristic equation  $F(x, T) = 0$  will be denoted by symbol  $x$ . That root which lies in the interval  $(0, 1)$  will be denoted in the following by symbol  $x_1^1$ . Remaining roots, which lie outside the interval  $(0, 1)$ , have no physical meaning for our purpose and therefore they will be neglected.

The course of the liquidus line yielded by the characteristic equation will be obtained in the following manner: for a certain series of temperatures  $T \in (T_1^f, T_2^f)$  we compute coefficients in characteristic equation (8) and find its root in the interval  $(0, 1)$ . Generally it is the solution of a higher-order equation and therefore it is found on a computer by some numerical method.

Then we compute from (7) the composition of solidus  $x_1^s$  and obtain a series of ordered pairs  $\{(T, x_1^l), (T, x_1^s)\}$ , which serve as a table of required functions  $x_1^l = f_1(T)$ ,  $x_1^s = f_2(T)$  on the interval  $(T_2^f, T_1^f)$ .

Formally, the characteristic equation might be constructed for an arbitrary type of functional dependence  $a = \varphi(x)$ . It depends on the form of functions (3), i.e. on relations expressing the dependence of the activity on the composition of the given component both in the liquid and in the solid solution, whether the implicit function  $T = f(x)$  will be determined by an equation constructed in this manner.

The function  $T = f(x)$  is determined implicitly by the equation  $F(x, T) = 0$  in the vicinity of point  $(x_0, T_0)$  for which it holds  $F(x_0, T_0) = 0$  and at which  $\partial F / \partial T \neq 0$ . The first derivative of function  $T = f(x)$ , which is given implicitly by the equa-

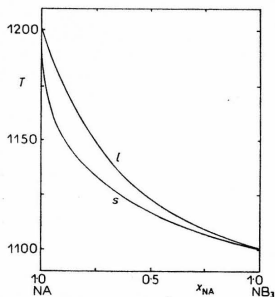


FIG. 1

The Phase Diagram of the NA—NB<sub>3</sub> System with a Common Ion and the Validity of the Temkin Functional Relation between the Activity and Composition for the Liquidus and with a Classically Ideal Behaviour of the Solidus

$T_1^f = 1200$  K,  $T_2^f = 1100$  K,  $\Delta H_1^f = 126$  kJ mol<sup>-1</sup> (= 30 kcal mol<sup>-1</sup>),  $\Delta H_2^f = 21$  kJ . mol<sup>-1</sup> (= 5 kcal mol<sup>-1</sup>), l liquidus curve, s solidus curve.

tion  $F(x, T) = 0$ , is equal to<sup>6</sup>

$$\frac{dT}{dx} = - \frac{\partial F / \partial x}{\partial F / \partial T}. \quad (9)$$

For characteristic equation (8) it holds

$$\frac{\partial F}{\partial x_1^1} = Q \frac{d\psi_2}{dx_1^s} \frac{\partial x_1^s}{\partial x_1^1} - \frac{d\varphi_2}{dx_1^1} \quad (10)$$

$$\frac{\partial F}{\partial T} = \frac{Q}{RT^2} \left[ \Delta H_2^f \psi_2(x_1^s) + M \Delta H_1^f \frac{d\psi_2}{dx_1^s} \frac{\partial x_1^s}{\partial M} \right].$$

Values of functions  $M$  and  $Q$  at the boundary points of the interval ( $T_1^f, T_2^f$ ) are equal to

$$Q(T_2^f) = 1 \quad Q(T_1^f) = \exp \left[ \frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T_1^f} \right) \right] = Q_0, \quad (11)$$

$$M(T_2^f) = \exp \left[ \frac{\Delta H_1^f}{R} \left( \frac{1}{T_1^f} - \frac{1}{T_2^f} \right) \right] = M_0 \quad M(T_1^f) = 1. \quad (12)$$

Since from (4) it follows  $\lim_{T \rightarrow T_1^f} \psi_2(x_1^s) = 0$  (for  $T \rightarrow T_1^f$ ), we obtain the following limiting relations:

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^1} = R(T_1^f)^2 \left[ \lim_{T \rightarrow T_1^f} \frac{d\varphi_2}{dx_1^1} - Q_0 \lim_{T \rightarrow T_1^f} \frac{d\psi_2}{dx_1^s} \lim_{T \rightarrow T_1^f} \frac{\partial x_1^s}{\partial x_1^1} \right] \cdot \left[ Q_0 \Delta H_1^f \lim_{T \rightarrow T_1^f} \frac{d\psi_2}{dx_1^s} \lim_{T \rightarrow T_1^f} \frac{\partial x_1^s}{\partial M} \right]^{-1}. \quad (13)$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^1} = R(T_2^f)^2 \left[ \lim_{T \rightarrow T_2^f} \frac{d\varphi_2}{dx_1^1} - \lim_{T \rightarrow T_2^f} \frac{d\psi_2}{dx_1^s} \lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial x_1^1} \right] \cdot \left[ \Delta H_2^f + M_0 \Delta H_1^f \lim_{T \rightarrow T_2^f} \frac{d\psi_2}{dx_1^s} \lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial M} \right]^{-1}. \quad (14)$$

By differentiating relation (7) we get

$$\frac{dx_1^s}{dT} = \frac{\partial x_1^s}{\partial M} \frac{dM}{dT} + \frac{\partial x_1^s}{\partial x_1^1} \frac{dx_1^1}{dT}$$

which can be rearranged to give

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^s} = Q_0 \lim_{T \rightarrow T_1^f} \frac{d\psi_2/dx_1^s}{d\varphi_2/dx_1^s} \lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^s}, \quad (15)$$

$$\begin{aligned} \lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s} &= \left[ \Delta H_2^f + M_0 \Delta H_1^f \lim_{T \rightarrow T_2^f} \frac{d\psi_2}{dx_1^s} \lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial M} \right] \\ &\cdot \left[ \Delta H_2^f \lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial x_1^s} + M_0 \Delta H_1^f \lim_{T \rightarrow T_2^f} \frac{d\varphi_2}{dx_1^s} \lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial M} \right]^{-1} \lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s}. \end{aligned} \quad (16)$$

#### EXAMPLE

If we assume that in a system of type  $N_p A_q - N_r B_t$  with a common ion the Temkin functional relation<sup>7,8</sup> between activity and composition holds for the liquidus and that the behaviour of the solidus is classically ideal, relations (3) take the form of

$$\begin{aligned} a_1^l &= \varphi_1(x_1^l) = \left[ \frac{qx_1^l}{t + x_1^l(q-t)} \right]^q & a_1^s &= \psi_1(x_1^s) = x_1^s \\ a_2^l &= \varphi_2(x_1^l) = \left[ \frac{t(1-x_1^l)}{t + x_1^l(q-t)} \right]^t & a_2^s &= \psi_2(x_1^s) = 1 - x_1^s. \end{aligned}$$

Relation (7) changes to

$$x_1^s = \Phi(M, x_1^l) = \frac{1}{M} \left[ \frac{qx_1^l}{t + x_1^l(q-t)} \right]^q$$

and characteristic equation (8) to

$$MQ - Q \left[ \frac{qx_1^l}{t + x_1^l(q-t)} \right]^q - M \left[ \frac{t(1-x_1^l)}{t + x_1^l(q-t)} \right]^t = 0$$

$$\frac{d\varphi_2}{dx_1^l} = t \left[ \frac{t(1-x_1^l)}{t + x_1^l(q-t)} \right]^{t-1} \frac{(-t)q}{[t + x_1^l(q-t)]^2}$$

$$\frac{d\psi_2}{dx_1^s} = -1 \quad \frac{\partial x_1^s}{\partial M} = -\frac{1}{M^2} \left[ \frac{qx_1^l}{t + x_1^l(q-t)} \right]^q$$

$$\frac{\partial x_1^s}{\partial x_1^l} \frac{1}{M} q \left[ \frac{qx_1^l}{t + x_1^l(q-t)} \right]^{q-1} \frac{qt}{[t + x_1^l(q-t)]^2}.$$

The corresponding limiting values of the derivatives are equal to

$$\lim_{T \rightarrow T_1^f} \frac{d\varphi_2}{dx_1^1} = \begin{cases} 0 & \text{for } t > 1 \\ -1/q & \text{for } t = 1 \end{cases}$$

$$\lim_{T \rightarrow T_1^f} \frac{d\psi_2}{dx_1^s} = -1 \quad \lim_{T \rightarrow T_1^f} \frac{\partial x_1^s}{\partial x_1^1} = t \quad \lim_{T \rightarrow T_1^f} \frac{\partial x_1^s}{\partial M} = -1$$

$$\lim_{T \rightarrow T_2^f} \frac{d\varphi_2}{dx_1^1} = -q \quad \lim_{T \rightarrow T_2^f} \frac{d\psi_2}{dx_1^s} = -1$$

$$\lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial x_1^1} = \begin{cases} 0 & \text{for } q > 1 \\ 1/(M_0 t) & \text{for } q = 1 \end{cases} \quad \lim_{T \rightarrow T_2^f} \frac{\partial x_1^s}{\partial M} = 0,$$

Then Eqs (13)–(16) assume the form of

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^1} = \begin{cases} tR(T_1^f)^2/\Delta H_1^f & \text{for } t > 1 \\ (qQ_0 - 1)R(T_1^f)^2/(qQ_0 \Delta H_1^f) & \text{for } t = 1 \end{cases}$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^1} = \begin{cases} -qR(T_2^f)^2/\Delta H_2^f & \text{for } q > 1 \\ (1 - M_0 t)R(T_2^f)^2/(tM_0 \Delta H_2^f) & \text{for } q = 1 \end{cases}$$

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^s} = \begin{cases} +\infty & \text{for } t > 1 \\ (qQ_0 - 1)R(T_1^f)^2/\Delta H_1^f & \text{for } t = 1 \end{cases}$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s} = \begin{cases} -\infty & \text{for } q > 1 \\ (1 - M_0 t)R(T_2^f)^2/\Delta H_2^f & \text{for } q = 1. \end{cases}$$

The phase diagram of a concrete solution of this type for  $q = 1$ ,  $t = 3$  and for the following choice of values  $T_1^f = 1200$  K,  $T_2^f = 1100$  K,  $\Delta H_1^f = 126$  kJ mol<sup>-1</sup> (= 30 kcal . mol<sup>-1</sup>),  $\Delta H_2^f = 21$  kJ mol<sup>-1</sup> (= 5 kcal mol<sup>-1</sup>) is on Fig. 1.

#### Case without the Characteristic Equation

The course of liquidus and solidus lines can be obtained by solving the set of Eqs (5), (6) for different values of the temperature  $T \in (T_1^f, T_2^f)$ . Since it is a nonlinear set of equations, it will be solved by a numerical method.

For the computation of tangent slopes we will employ a property following from Eqs (5), (6), namely that quantities  $M$  and  $Q$  depend on temperature  $T$  through variables  $x_1^1$  and  $x_1^s$

$$M = f(x_1^1, x_1^s) \quad Q = g(x_1^1, x_1^s) \quad x_1^1 = f_1(T) \quad x_1^s = f_2(T).$$

According to the rule for differentiating composite functions it holds

$$\begin{aligned}\frac{dM}{dT} &= \frac{\partial f}{\partial x_1^1} \frac{dx_1^1}{dT} + \frac{\partial f}{\partial x_1^s} \frac{dx_1^s}{dT} \\ \frac{dQ}{dT} &= \frac{\partial g}{\partial x_1^1} \frac{dx_1^1}{dT} + \frac{\partial g}{\partial x_1^s} \frac{dx_1^s}{dT}.\end{aligned}\quad (17)$$

By differentiating functions (1) and (2) with respect to  $T$  we obtain a set of linear algebraic equations in unknown derivatives  $dx_1^1/dT$  and  $dx_1^s/dT$ . This set will be solved by the Cramer rule.

$$\begin{aligned}\frac{\partial f}{\partial x_1^1} \frac{dx_1^1}{dT} + \frac{\partial f}{\partial x_1^s} \frac{dx_1^s}{dT} &= M \frac{\Delta H_1^f}{RT^2} \\ \frac{\partial g}{\partial x_1^1} \frac{dx_1^1}{dT} + \frac{\partial g}{\partial x_1^s} \frac{dx_1^s}{dT} &= Q \frac{\Delta H_2^f}{RT^2}.\end{aligned}$$

Determinant  $J$  of this set is Jacobi's functional determinant

$$J = \begin{vmatrix} \frac{\partial f}{\partial x_1^1} & \frac{\partial f}{\partial x_1^s} \\ \frac{\partial g}{\partial x_1^1} & \frac{\partial g}{\partial x_1^s} \end{vmatrix}\quad (18)$$

Further it holds

$$J_{x_1^1} = \begin{vmatrix} M \frac{\Delta H_1^f}{RT^2} & \frac{\partial f}{\partial x_1^s} \\ Q \frac{\Delta H_2^f}{RT^2} & \frac{\partial g}{\partial x_1^s} \end{vmatrix} \quad J_{x_1^s} = \begin{vmatrix} \frac{\partial f}{\partial x_1^1} & M \frac{\Delta H_1^f}{RT^2} \\ \frac{\partial g}{\partial x_1^1} & Q \frac{\Delta H_2^f}{RT^2} \end{vmatrix}.\quad (19)$$

The required derivatives are then equal to

$$dT/dx_1^1 = J/J_{x_1^1} \quad dT/dx_1^s = J/J_{x_1^s}.$$

This method for computing the derivatives will be denoted as the method of Jacobians. In our case



$$J = \begin{vmatrix} \varphi'_1(x_1^l) & -\varphi_1(x_1^l) \psi'_1(x_1^s) \\ \psi_1(x_1^s) & \Psi_1^2(x_1^s) \\ \varphi'_2(x_1^l) & -\varphi_2(x_1^l) \psi'_2(x_1^s) \\ \psi_2(x_1^s) & \Psi_2^2(x_1^s) \end{vmatrix}$$

where  $\varphi'_1(x_1^l) = d\varphi_1(x_1^l)/dx_1^l$  etc. After the computation of the determinants and a rearrangement we obtain:

$$\frac{dT}{dx_1^l} = \frac{ART^2}{-MQ \Delta H_1^f \psi'_2(x_1^s) \psi_1(x_1^s) + MQ \Delta H_2^f \psi'_1(x_1^s) \psi_2(x_1^s)} \quad (20)$$

$$\frac{dT}{dx_1^s} = \frac{ART^2}{Q \Delta H_2^f \varphi'_1(x_1^l) \psi_2(x_1^s) - M \Delta H_1^f \varphi'_2(x_1^l) \psi_1(x_1^s)} \quad (21)$$

where  $A = -Q\varphi'_1(x_1^l) \psi'_2(x_1^s) + M\varphi'_2(x_1^l) \psi'_1(x_1^s)$ . By performing the limit of relation (20) for  $T \rightarrow T_1^f$  and then for  $T \rightarrow T_2^f$  and taking into account conditions (4) we get:

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^l} = - \frac{1}{Q_0 \Delta H_1^f} \lim_{T \rightarrow T_1^f} \frac{A}{\psi'_2(x_1^s)} R(T_1^f)^2 \quad (22)$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^l} = \frac{1}{M_0 \Delta H_2^f} \lim_{T \rightarrow T_2^f} \frac{A}{\psi'_1(x_1^s)} R(T_2^f)^2 \quad (23)$$

Analogically, by performing the limits for relation (21) we obtain:

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^s} = - \frac{1}{\Delta H_1^f} \lim_{T \rightarrow T_1^f} \frac{A}{\varphi'_2(x_2^l)} R(T_1^f)^2 \quad (24)$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s} = - \frac{1}{\Delta H_2^f} \lim_{T \rightarrow T_2^f} \frac{A}{\varphi'_1(x_1^l)} R(T_2^f)^2. \quad (25)$$

#### EXAMPLE

On solving a  $M_pA_q-N_rB_t$  system without a common ion and for which the Temkin functional relation between activity and composition holds for both the liquidus and the solidus, relations (3) take the form of

$$a_1^l = \varphi_1(x_1^l) = \left[ \frac{px_1^l}{r + x_1^l(p - r)} \right]^p \left[ \frac{qx_1^l}{t + x_1^l(q - t)} \right]^q$$

$$a_2^1 = \varphi_2(x_1^1) = \left[ \frac{r(1-x_1^1)}{r+x_1^1(p-r)} \right]^r \left[ \frac{t(1-x_1^1)}{t+x_1^1(q-t)} \right]^t.$$

Analogous relations hold also for the solidus. The characteristic equation cannot be constructed for this case. Therefore we compute limiting values of tangent slopes at melting points of pure components by the method of Jacobians with the following results:

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^1} = \frac{(r+t)(Q_0^{1/(r+t)} - 1)}{\Delta H_1^f Q_0^{1/(r+t)}} R(T_1^f)^2$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^1} = \frac{(p+q)(1 - M_0^{1/(p+q)})}{\Delta H_2^f M_0^{1/(p+q)}} R(T_2^f)^2$$

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^s} = Q_0^{1/(r+t)} \lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^1}$$

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s} = M_0^{1/(p+q)} \lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^1}.$$

By considering (11) and (12), for  $T_1^f > T_2^f$  it holds  $Q_0 > 1 \wedge M_0 < 1$  and for  $T_1^f < T_2^f$  it holds  $Q_0 < 1 \wedge M_0 > 1$ . In both cases the limiting values of tangent slopes of both the liquidus and solidus lines possess identical signs at  $T = T_1^f$  and  $T = T_2^f$ , which confirms the monotonicity of these lines.

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