

# Equilibrium "solidus—liquidus" in binary systems having complete miscibility in the solid state

## Type I after Roozeboom\*

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The thermodynamic analysis of the course of liquidus and solidus curves in binary systems having complete miscibility in both liquid and solid states was carried out. The binary systems of the type NA—NB<sub>t</sub> with common ion were considered. The object of the treatment was the so-called type I after Roozeboom (both liquidus and solidus curves have a monotonous course). It is assumed that the liquid solution obeys the Temkin ideal model and the solid one the classic ideal model.

Let us denote the component NA as "1", the component NB<sub>t</sub> as "2". The figures 1 and 2 will be used also as distinguishing indices at parameters  $T^f$ ,  $\Delta H_1^f$ ,  $a^s$ ,  $x^s$ ,  $a^l$ ,  $x^l$ . Then it can be proved that the thermodynamic conditions for the existence of such systems are as follows

$$T_1^f > T_2^f,$$
$$\Delta H_1^f > R \frac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t.$$

A relation which enables one to calculate the value of the enthalpy of fusion  $\Delta H_1^f$  of component "1" was derived. It is only necessary to know the value of the slopes of tangents to liquidus and solidus curves at the melting point  $T_2^f$  of component "2".

The equations describing the shape of liquidus and solidus curves in binary systems having complete miscibility of components in both liquid and solid states have been derived by *van Laar* [1]. The thermodynamic analysis of these equations, in the main with respect to the physical meaning of the slopes of tangents to liquidus and solidus curves for  $x \rightarrow 0$  and  $x \rightarrow 1$ , was carried out in [2]. It was assumed that the activities

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of both components were identical with their concentrations and therefore the Stortenberg factors  $k_{1/2}^{St}$  and  $k_{2/1}^{St}$  were equal to one [2]. As it has been shown [2], for the activities of both components and the corresponding temperature one may set

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

$$\ln \frac{a_2^l}{a_2^s} = \frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T} \right). \quad (2)$$

In eqns (1) and (2) the values of the change of enthalpy in the process "solidus—liquidus" are constant for both components, *i.e.*

$$\Delta H_1^{l/s} = \Delta H_1^f = \text{const} > 0, \quad (3)$$

$$\Delta H_2^{l/s} = \Delta H_2^f = \text{const} > 0. \quad (4)$$

This assumption (which is equivalent to the requirement  $\Delta C_p^{l/s} = 0$ ) is fulfilled with satisfaction practically for all substances unless the difference between their temperatures of fusion  $T_1^f$  and  $T_2^f$  is too great.

In this work, binary molten systems with common ion of the type NA—NB<sub>t</sub> having  $k_{2/1}^{St} = t$ ,  $k_{1/2}^{St} = 1$  were investigated (N = cation or anion, A, B = ions of opposite sign of charge with respect to N,  $t > 1$ ).

The Stortenberg correction factor  $k_{2/1}^{St}$  is equal to the number of new (foreign) particles (also ions) which arise in the system formed by the pure substance "1" as a result of introducing one molecule of the substance "2". An analogous definition holds for  $k_{1/2}^{St}$ .

We shall assume that:

1. The behaviour of liquid phase can be described by the Temkin model of ideal ionic solutions [3–5]. Then it holds

$$a_1^l = \frac{x_1^l}{t - x_1^l(t - 1)}, \quad (5)$$

$$a_2^l = \left[ \frac{t x_2^l}{1 + x_2^l(t - 1)} \right]^t, \quad (6)$$

where  $a_1^l$ ,  $x_1^l$  are the activity and mole fraction of the first component (*i.e.* NA) in the liquid solution and  $a_2^l$ ,  $x_2^l$  are the same parameters of the second component. It holds  $x_1^l + x_2^l = 1$ .

2. The solid solution of components "1" and "2" is classically ideal, *i.e.*

$$a_1^s = x_1^s, \quad (7)$$

$$a_2^s = x_2^s, \quad (8)$$

where  $a_1^s$ ,  $x_1^s$ ,  $a_2^s$ ,  $x_2^s$  are the activities and mole fractions, resp., of components in the solid solution;  $x_1^s + x_2^s = 1$ .

We shall introduce the functions  $M$  and  $Q$  which are defined as follows:

$$M = \frac{a_1^l}{a_1^s} = \frac{x_1^l}{x_1^s[t - x_1^l(t - 1)]} = \exp \left[ \frac{\Delta H_1^f}{R} \left( \frac{1}{T_1^f} - \frac{1}{T} \right) \right], \quad (9)$$

$$Q = \frac{a_2^1}{a_2^s} = \frac{t^t(1-x_1^1)^t}{(1-x_1^s)[t-x_1^1(t-1)]^t} = \exp \left[ \frac{\Delta H_2^f}{R} \left( \frac{1}{T_2^f} - \frac{1}{T} \right) \right]. \quad (10)$$

Because it is a binary system which is discussed, it has to be valid that  $T \neq T_1^f$  and  $T \neq T_2^f$  and therefore  $T$  can take only the values from the open interval  $(T_1^f; T_2^f)$ . However in binary systems it must also hold

$$\lim_{T \rightarrow T_2^f} x_1^1 = 0; \quad \lim_{T \rightarrow T_1^f} x_1^1 = 1.$$

Thus in our considerations we shall identify for briefness the limit with the functional value of mole fraction in terminal points of the interval  $\langle 0;1 \rangle$ , i.e. the temperature  $T$  will be chosen from the closed interval  $\langle T_1^f; T_2^f \rangle$ .

From (9) it follows

$$x_1^s = \frac{x_1^1}{M[t - x_1^1(t-1)]}. \quad (11)$$

After substituting  $x_1^s$  from (11) into (10) an algebraic equation of the  $t$ -th degree is obtained

$$Q[Mt - x(Mt - M + 1)][t - x(t-1)]^{t-1} - t^t M(1-x)^t \equiv F(x, T);$$

$$F(x, T) = 0. \quad (12)$$

The equation has  $t$  roots which are in the equation denoted as  $x$  instead of  $x_1^1$ . With respect to the physical unambiguosness only one of them can be located in the interval  $\langle 0;1 \rangle$ . This physically real root will be denoted again as  $x_1^1$ .

The degree of eqn (12) is identical with the number of ions of the second component which are not present in the first component. It equals therefore  $k_{2/1}^{St}$ . Eqn (12) holds also for  $t = 1$ . In this case it follows from (5) and (6)

$$a_1^1 = x_1^1,$$

$$a_2^1 = x_2^1,$$

i.e., the Temkin model provides for the type NA-NB the same relations as the classic model. The coefficients in eqn (12) are functions of the temperature  $T \in \langle T_1^f; T_2^f \rangle$ , enthalpies of fusion  $\Delta H_1^f$ ,  $\Delta H_2^f$ , temperatures of fusion  $T_1^f$ ,  $T_2^f$  and of the parameter  $t$ . For each temperature  $T \in \langle T_1^f; T_2^f \rangle$  we obtain an equation with different coefficients and therefore with other roots as well.

As it has been mentioned, if the Temkin model should be able to describe the monotonous course of liquidus and solidus curves in the interval  $\langle T_1^f; T_2^f \rangle$ , it must be just one root of eqn (12) from the interval  $\langle 0;1 \rangle$ . With a continuous change of temperature from  $T_1^f$  to  $T_2^f$  and in the opposite direction a continuous change of the root  $x_1^1$  in the interval  $\langle 0;1 \rangle$  must occur.

It is necessary to examine:

1. Whether eqn (12) has a root which equals zero or one regardless of the value of parameters  $t$ ,  $T_1^f$ ,  $T_2^f$ ,  $\Delta H_1^f$ ,  $\Delta H_2^f$ .

2. Whether eqn (12) has a root which equals zero for  $T = T_2^f$  and under what conditions will be the root positive for  $T \in \langle T_1^f; T_2^f \rangle$  and  $T \neq T_2^f$ .

3. Whether eqn (12) has a root which equals one for  $T = T_1^f$  and under what conditions is this root lower than one for  $T \in \langle T_1^f; T_2^f \rangle$  and  $T \neq T_1^f$ .

4. What are the slopes of tangents to liquidus and solidus curves for  $x_1 \rightarrow 0$  and  $x_1 \rightarrow 1$ .

*Ia. Investigation of the existence of a root which is equal to zero for  $T = T_2^f$* 

For  $T = T_2^f$ , taking into account (9) and (10),  $Q = 1$ ,

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

Then eqn (12) can be written as

$$[M_0 t - x(M_0 t - M_0 + 1)] [t + x(1 - t)]^{t-1} - t^t M_0 (1 - x)^t = 0. \quad (13)$$

The expressions  $[t + x(1 - t)]^{t-1}$  and  $(1 - x)^t$  can be raised to power by means of the binomial expansion:

$$\begin{aligned} [t + x(1 - t)]^{t-1} &= \binom{t-1}{0} t^{t-1} + \binom{t-1}{1} t^{t-2} [x(1 - t)] + \dots + \binom{t-1}{t-1} [x(1 - t)]^{t-1} = \\ &= t^{t-1} + x \Psi_1(x), \end{aligned}$$

where  $\Psi_1(x)$  is the  $(t - 2)$ nd degree polynomial.

Similarly

$$(1 - x)^t = 1 + x \Psi_2(x),$$

where  $\Psi_2(x)$  is the polynomial of the  $(t - 1)$ st degree.

Then eqn (13) results in

$$[M_0 t - x(M_0 t - M_0 + 1)] [t^{t-1} + x \Psi_1(x)] - t^t M_0 [1 + x \Psi_2(x)].$$

After multiplication and simplifying we obtain

$$\begin{aligned} x[-(M_0 t - M_0 + 1) t^{t-1} + M_0 t \Psi_1(x) - (M_0 t - M_0 + 1) x \Psi_1(x) - \\ - t^t M_0 \Psi_2(x)] \equiv x \Phi(x) = 0, \end{aligned} \quad (14)$$

where  $\Phi(x)$  is the polynomial of the  $(t - 1)$ st degree.

From eqn (14) it can be seen that for  $T = T_2^f$  eqn (12) has one root which is equal to zero regardless of the value of the parameters  $t$ ,  $T_1^f$ ,  $T_2^f$ ,  $\Delta H_1^f$ ,  $\Delta H_2^f$ .

We shall examine further a possibility of a multiple root of eqn (12) which equals zero.

A necessary and sufficient condition which is to be fulfilled in order that a number  $\alpha$  would be the  $r$ -fold root of an equation  $f(x) = 0$  is as follows ([6], p. 67):

$$f(\alpha) = f'(\alpha) = \dots = f^{(r-1)}(\alpha) = 0 \quad \text{but} \quad f^{(r)}(\alpha) \neq 0.$$

Let us consider the first two derivatives of eqn (13)

$$\begin{aligned} F'(x, T_2^f) &= -[M_0 t - M_0 + 1] [t - x(t - 1)]^{t-1} + \\ &+ [M_0 t - x(M_0 t - M_0 + 1)] (t - 1) [t - x(t - 1)]^{t-2} [-(t - 1)] + t^{t+1} M_0 (1 - x)^{t-1}, \\ F''(x, T_2^f) &= 2[M_0 t - M_0 + 1] (t - 1)^2 [t - x(t - 1)]^{t-2} + \\ &+ [M_0 t - x(M_0 t - M_0 + 1)] (t - 1)^3 (t - 2) [t - x(t - 1)]^{t-3} - \\ &- t^{t+1} (t - 1) M_0 (1 - x)^{t-2}. \end{aligned}$$

After rearrangement and setting  $x = 0$  we obtain

$$F'(0, T_2^f) = M_0 t - t^{t-1}, \quad (15)$$

$$F''(0, T_2^f) = t^{t-2}(t-1) [M_0 t(-2t+1) + 2(t-1)]. \quad (16)$$

For  $F'(0, T_2^f) = 0$ , it follows from eqn (15)

$$M_0 = t^{-1} \quad (17)$$

or after taking the logarithm

$$\Delta H_1^f = R \frac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t. \quad (18)$$

With respect to eqn (9) the function  $M$  equals one only for  $T = T_1^f$ . Eqn (17) cannot be satisfied for  $t = 1$  what means that eqn (12) cannot have a double root which equals zero at the point  $T = T_2^f$  in the case of the solution of the type NA-NB.

Substituting eqn (17) into eqn (16) we obtain

$$F''(0, T_2^f)_{M=t^{-1}} = -t^{t-2}(t-1). \quad (19)$$

It is obvious that for  $t > 1$ ,  $F''(0, T_2^f)_{M=t^{-1}}$  is always different from zero and it follows that eqn (12) has for  $T = T_2^f$  and for valid relation (17) a double root which equals zero regardless of the degree of this equation.

Let us have a look at the geometrical and physical meaning of the double root which is equal to zero.

Let us consider eqn (12) to be a function  $T = f(x)$  which is given implicitly in the interval  $\langle 0;1 \rangle$  by the equation  $F(x, T) = 0$  ([7], p. 377). Then

$$\frac{dT}{dx} = - \frac{\frac{\partial F}{\partial x}}{\frac{\partial F}{\partial T}} \quad (20)$$

with

$$\frac{\partial F}{\partial T} = \left\{ MQt \frac{\Delta H_1^f}{RT^2} + MQt \frac{\Delta H_2^f}{RT^2} + x \left[ QM \frac{\Delta H_2^f}{RT^2} + QM \frac{\Delta H_1^f}{RT^2} - Q \frac{\Delta H_2^f}{RT^2} - tMQ \frac{\Delta H_1^f}{RT^2} - tMQ \frac{\Delta H_2^f}{RT^2} \right] \right\} \left[ t + x(1-t) \right]^{t-1} - M \frac{\Delta H_1^f}{RT^2} t^{t(1-x)t}, \quad (21)$$

$$\frac{\partial F}{\partial x} = Q(M-1-Mt) [t+x(1-t)]^{t-1} + Q[Mt-x(Mt-M+1)] (t-1) \cdot [t+x(1-t)]^{t-2}(1-t) + t^{t+1}(1-x)^{t-1} M.$$

With respect to eqn (20)

$$\left[ \frac{dT}{dx} \right]_{T=T_2^f} = 0 \text{ if } \left[ \frac{\partial F}{\partial x} \right]_{T=T_2^f} = 0$$

and simultaneously

$$\left[ \frac{\partial F}{\partial T} \right]_{T=T_2^f} \neq 0.$$

However, the symbol  $\left[ \frac{\partial F}{\partial x} \right]_{T=T_2^f}$  has the same meaning as the symbol  $F'(x, T_2^f)$ .

Because

$$\left[ \frac{\partial F}{\partial T} \right]_{T=T_2^f} = M_0 t^t \frac{\Delta H_2^f}{R(T_2^f)^2},$$

and this expression differs from zero for each  $t$ , the equation  $F'(x, T_2^f) = 0$  is equivalent to the equation

$$\left[ \frac{dT}{dx} \right]_{T=T_2^f} = 0.$$

If at the same time  $\frac{d^2T}{dx^2} \neq 0$  at the point  $T = T_2^f$ , the function  $T = f(x)$  has an extremum at the point  $T = T_2^f$ .

According to [7] (p. 378, eqn (4)),  $\frac{d^2T}{dx^2} = 0$  if  $\frac{\partial^2 F}{\partial x^2} = 0$  and  $\frac{\partial F}{\partial y} \neq 0$ . The symbol

$\left[ \frac{\partial^2 F}{\partial x^2} \right]_{T=T_2^f, x=0}$  is equivalent to the symbol  $F''(0, T_2^f)$ . According to eqn (19) this expression differs from zero for each  $t > 1$ . It follows from this that the double zero point of the equation  $F(x, T) = 0$  is simultaneously the extremum of the function  $T = f(x)$  which is defined in the interval  $\langle 0; 1 \rangle$  implicitly by the equation  $F(x, T) = 0$ . The extremum is at the point  $T = T_2^f$ .

### *1b. Examination of the existence of the root which equals one at $T = T_1^f$*

For  $T = T_1^f$ ,  $M = 1$ ,

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

Thus eqn (12) results in

$$Q_0 [t + x(-t)] [t + x(1-t)]^{t-1} - t^t (1-x)^t = 0$$

and after simplifying

$$(1-x) [Q_0 t \{t + x(1-t)\}^{t-1} - t^t] = 0. \quad (22)$$

From the expression (22) it can be seen that for  $T = T_1^f$ , the equation has a root  $x_1^1 = 1$  regardless of the value of the parameters  $t$ ,  $T_1^f$ ,  $T_2^f$ ,  $\Delta H_1^f$ ,  $\Delta H_2^f$ .

In addition we shall examine the possibility of a double root of eqn (12) at  $T = T_1^f$  which equals one.

$$F'(x, T_1^f) = -tQ_0 [t + x(1-t)]^{t-1} + Q_0(t-tx)(t-1) [tx(1-t)]^{t-2} + t^{t+1}(1-x)^{t-1}.$$

A necessary condition for the existence of the double root which is equal to one at  $T = T_1^f$  may be given as  $F'(1, T_1^f) = 0$ .

$$F'(1, T_1^f) = -tQ_0[t + 1 - t]^{t-1} = -tQ_0 = 0. \quad (23)$$

However, the condition (23) cannot be satisfied because both terms of the product  $tQ_0$  differ from zero. Hence eqn (12) has for  $T = T_1^f$  only a simple root  $x = 1$ , *i.e.* the relation based on the Temkin model cannot have an extremum at the point  $T = T_1^f$ .

Consequently eqn (12) has for  $T = T_2^f$  a simple root which equals zero and for  $T = T_1^f$  a simple root which equals one regardless of the magnitude of the parameters  $t$ ,  $T_1^f$ ,  $T_2^f$ ,  $\Delta H_1^f$ ,  $\Delta H_2^f$ . If the value of the enthalpy of fusion  $\Delta H_1^f$  is given by the expression (18) then the equation has a double root which equals zero. The double root which equals one cannot exist if we use the Temkin model.

## 2. Examination of the conditions having influence on the sign of the differential $dx$ at the point $T = T_2^f$

With respect to the relations (20) and (21) one obtains for  $T = T_2^f$ :

$$\left[ \frac{dT}{dx} \right]_{T=T_2^f} = \frac{R(T_2^f)^2 \cdot (1 - M_0t)}{tM_0\Delta H_2^f} \quad (24)$$

or

$$[dx]_{T=T_2^f} = dx_0 = \frac{tM_0\Delta H_2^f}{R(T_2^f)^2 \cdot (1 - M_0t)} dT.$$

If  $1 - M_0t = 0$  and hence if the relation (17) or (18) is valid (what is equivalent to the existence of a double root of eqn (12) which is equal to zero) then the relation (24) shows that the first derivative of the liquidus curve at the point  $T = T_2^f$  equals zero. Taking

into account the non-zero derivative  $\left[ \frac{dT}{dx} \right]_{T=T_2^f}$  we have to consider two cases:

$$2a. T_1^f > T_2^f$$

In this case, if we require a monotonous course of liquidus curve inside the interval  $\langle T_1^f; T_2^f \rangle$ , it must be valid  $\left[ \frac{dT}{dx} \right]_{T=T_2^f} > 0$ , *i.e.*

$$1 - M_0t > 0$$

and after rearrangement

$$\Delta H_1^f > R \frac{T_1^f T_2^f}{T_1^f - T_2^f} \ln t. \quad (25)$$

With respect to this condition the increment  $dx_0$  is positive when temperature increases from  $T_2^f$  by  $dT$ , *i.e.* the root of eqn (12) is shifted inward the interval  $\langle 0; 1 \rangle$  this being in agreement with the requirement of physical reality. The condition (25) can be expressed as a function of the difference of temperatures of fusion  $\Delta T = T_1^f - T_2^f$  as follows:

$$\Delta H_1^f > RT_2^f \left[ \frac{T_2^f}{\Delta T} + 1 \right] \ln t. \quad (25a)$$

The higher is the difference of temperatures of fusion  $\Delta T$  and the lower is the temperature

of fusion of the second component  $T_2^f$ , the lower will be the critical value of the enthalpy of fusion  $\Delta H_1^f$  in order to satisfy the inequality (25a).

2b.  $T_1^f < T_2^f$

For satisfying a monotonous course inside the interval  $\langle T_1^f; T_2^f \rangle$  the following condition is to be fulfilled

$$\left[ \frac{dT}{dx} \right]_{T=T_1^f} < 0, \quad \text{i.e. } 1 - M_0 t < 0$$

and after rearrangement

$$\Delta H_1^f > -R \frac{T_1^f T_2^f}{T_2^f - T_1^f} \ln t. \tag{26}$$

For  $T_2^f - T_1^f > 0$  and  $t > 1$ , the expression on the right side of the inequality (26) is always negative and hence the inequality is always satisfied. For  $t = 1$ , the right side of the inequality (26) equals zero. In this case the Temkin model gives the same relations as the classic one. There is no limiting condition for the magnitude of  $\Delta H_1^f$  excepting — in agreement with eqn (3) — that  $\Delta H_1^f > 0$ .

We may summarize the results of the item 2 as follows: Considering  $T_1^f > T_2^f$ , we obtain for  $T = T_2^f$  and for  $dT > 0$  a positive value of  $dx_0$ . It means that if  $\Delta H_1^f$  satisfies the condition (25) the root is shifted inward the interval  $\langle 0; 1 \rangle$ . For  $T_1^f < T_2^f$ ,  $dx_0$  is always positive. The latter result does not contradict the physical reality, too.

### 3. Examination of the conditions having influence on the sign of $dx$ at the point $T = T_1^f$

Let us consider again eqn (12) as a function  $T = f(x)$  which is given in the interval  $\langle 0; 1 \rangle$  implicitly by the equation  $F(x, T) = 0$ . With respect to (20) and (21) we obtain

$$[dx]_{T=T_1^f} = dx_1 = \frac{\Delta H_1^f}{tR(T_1^f)^2} dT. \tag{27}$$

In the next, we can distinguish two cases:

3a.  $T_1^f > T_2^f$

From eqn (27) it follows that  $dT$  and  $dx$  have the same sign at the point  $T = T_1^f$ . It means that if temperature falls from  $T_1^f$  by  $dT$  the value of the root decreases simultaneously by  $dx_1$ , being the condition of physical reality.

3b.  $T_1^f < T_2^f$ .

Physical reality requires  $dx < 0$  at an increase of temperature from  $T_1^f$  by  $dT$  what is in contrast to the relation (27).

These results show that the binary system of the type  $NA-NB_t$ , with a monotonous course of liquidus and solidus curves, which obeys the Temkin model in the liquid state and the classic model in the solid state can exist only if  $T_1^f > T_2^f$  and if in addition the inequality (25) or eqn (18) are satisfied.



4. Limit values of the slopes of tangents to liquidus and solidus curves at the melting points of pure components and their relationship to the enthalpies of fusion  $\Delta H_1^f$  and  $\Delta H_2^f$

We consider the root of eqn (12) which has the character of the mole fraction for all  $T \in \langle T_1^f; T_2^f \rangle$ . Thus we shall denote it in the next as  $x_1^l$ .

The relation (24) gives simultaneously

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx} = \frac{R(T_2^f)^2 \cdot (1 - tM_0)}{\Delta H_2^f t M_0}. \quad (28)$$

With respect to (11) it holds

$$\begin{aligned} \frac{dx_1^s}{dT} &= \frac{d}{dx} \left( \frac{x}{t - x_1^l(t-1)} \right) \cdot \frac{dx_1^l}{dT} \cdot \frac{1}{M} \cdot \frac{d}{dT} \left( \frac{1}{M} \right) \cdot \frac{x_1^l}{t - x_1^l(t-1)}, \\ \frac{dx_1^s}{dT} &= \frac{t}{[t - x_1^l(t-1)]^2} \cdot \frac{1}{M} \cdot \frac{dx_1^l}{dT} - \frac{1}{M^2} \cdot M \frac{\Delta H_1^f}{RT^2} \cdot \frac{x_1^l}{t - x_1^l(t-1)}. \end{aligned} \quad (29)$$

Taking the limit for  $T \rightarrow T_2^f$  we obtain:

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s} = \frac{R(T_2^f)^2}{\Delta H_2^f} \cdot (1 - tM_0) \quad (30)$$

or

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s} = tM_0 \lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^l}. \quad (31)$$

The relation (27) gives

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^l} = \frac{tR(T_1^f)^2}{\Delta H_1^f}. \quad (32)$$

With respect to (29) and (32) we have

$$\lim_{T \rightarrow T_1^f} \frac{dx_1^s}{dT} = \frac{t}{[t - t + 1]^2} \cdot \lim_{T \rightarrow T_1^f} \frac{dx_1^l}{dT} - \frac{\Delta H_1^f}{R(T_1^f)^2} \cdot \frac{1}{t - t + 1} = t \frac{\Delta H_1^f}{tR(T_1^f)^2} - \frac{\Delta H_1^f}{R(T_1^f)^2} = 0$$

and hence

$$\lim_{T \rightarrow T_1^f} \frac{dT}{dx_1^s} = +\infty. \quad (33)$$

If we are very close above the critical value of the enthalpy of fusion  $\Delta H_1^f$  (see (25)) where  $tM_0 \doteq 0$  then

$$\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^l} \doteq 0 \quad \text{for each } \Delta H_2^f.$$

As a result of that the liquidus and solidus curves have a similar course regardless of the value of the parameter  $\Delta H_2^f$ .

We shall introduce further a ratio of the limit values of the derivatives of liquidus and solidus curves at the point  $T = T_2^f$ .

$$k = \frac{\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^l}}{\lim_{T \rightarrow T_2^f} \frac{dT}{dx_1^s}} = \frac{1}{tM_0} = \frac{1}{t} \exp \left[ \frac{\Delta H_1^f (T_1^f - T_2^f)}{RT_1^f T_2^f} \right]. \quad (34)$$

The relation (34) does not depend on the magnitude of the enthalpy of fusion  $\Delta H_2^f$  of the second component. An analogous relation for the ratio of the limit values of derivatives at the melting point  $T_1^f$  of the first component equals zero because of eqn (33).

In the end it may be stated that the relations (32) and (34) allow to determine the enthalpy of fusion  $\Delta H_1^f$  of the first component having higher melting point in two different ways. This value is not known in many cases at all or only with a low accuracy. For the calculation we have to know the temperatures of fusion  $T_1^f$ ,  $T_2^f$  assuming  $T_1^f > T_2^f$  and the limit values of the slopes of tangents to liquidus and solidus curves at  $T = T_1^f$  or at  $T = T_2^f$ . The relation (34) is of particular interest. By means of it one is able to determine the value  $\Delta H_1^f$  only from the course of liquidus and solidus curves in the vicinity of the melting point  $T_2^f$  of the second component having a lower melting point.

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