

Liquidus Curves of Ideal Ionic Systems. II.

M. MALINOVSKÝ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
Bratislava 9*

Received March 11, 1969

Analysis of equations for calculation of liquidus curves in a binary simple eutectic system is performed. The equation of the slope of tangent to the liquidus curve in the melting point is derived and the relationship to the Stortenbeker correction factor is shown. Character of the liquidus curve with regard to its concavity or convexity with respect to the concentration axis is discussed. It has been found that convex parts of liquidus curves with regard to the concentration axis occur much more frequently in the ionic systems.

1. Analysis of equations for calculation of liquidus curves in a binary system. General rules

Let us consider a simple eutectic system $Q-Z$; for the activity of the first component along the liquidus curve the following is valid

$$d \ln a_Q = \frac{\Delta H_Q^f}{R} \cdot \frac{dT_Q}{T_Q^2} \quad (1)$$

where ΔH_Q^f is the molar enthalpy of melting of the component Q at T_Q ,

R is the universal gas constant per mole,

T_Q is temperature of the primary crystallization of the substance Q from the liquid solution $Q + Z$, wherein the activity of the substance Q equals a_Q .

Let the solution be ideal ($a_i = x_i$), and $\Delta H_Q^f = \text{const}$; integrating the equation (1) we obtain Le Chatelier—Schröder equation

$$\ln x_Q = \frac{\Delta H_Q^f}{R} \cdot \left[\frac{1}{T_Q^f} - \frac{1}{T_Q} \right] \quad (2)$$

where T_Q^f is the temperature of the melting point of the pure substance Q .

Rearranging the equation (2) we get

$$T_Q = \frac{\Delta H_Q^f}{\Delta S_Q^f - R \ln x_Q} \quad (3)$$

where $\Delta S_Q^f = \frac{\Delta H_Q^f}{T_Q^f}$ is the molar entropy of melting of the component Q .

Derivating equation (3) with respect to x_Q and limiting the new equation for $x_Q \rightarrow 1$ we get

$$\lim_{x_Q \rightarrow 1} \frac{dT_Q}{dx_Q} = \frac{R[T_Q^f]^2}{\Delta H_Q^f} = K_Q^{\text{td}} \quad (4)$$

where the quantity K_Q^{td} will be called the *constant of thermic depression* of the substance Q .

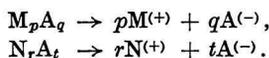
In case that the solution is not ideal we have to write the equation (3) as follows

$$T_Q = \frac{\Delta H_Q^f}{\Delta S_Q^f - R \ln a_Q} \quad (5)$$

2. Determination of slopes of tangents to the liquidus curve in the point $T_i = T_i^f$

2.1. Systems with one common ion

Let us consider the binary system $M_pA_q - N_rA_t$. We assume a complete dissociation of the components



Let the mole fractions of the first and second component be x_1 and x_2 , respectively. Then for the activities of the components the following is valid:

$$a_{M_pA_q} = \left[\frac{px_1}{r + x_1(p - r)} \right]^p, \quad (6)$$

$$a_{N_rA_t} = \left[\frac{rx_2}{p + x_2(r - p)} \right]^r. \quad (7)$$

Substituting the equation (6) in the equation (5) we get the following expression for the dependence of the temperature of primary crystallization of the first component T_1 on the composition

$$T_1 = \frac{\Delta H_1^f}{\Delta S_1^f - R \ln \left[\frac{px_1}{r + x_1(p - r)} \right]^p}. \quad (8)$$

Then

$$\lim_{x_1 \rightarrow 1} \frac{dT_1}{dx_1} = r R \frac{\Delta H_1^f}{[\Delta S_1^f]^2} = r \frac{R [T_1^f]^2}{\Delta H_1^f} \quad (9a)$$

or

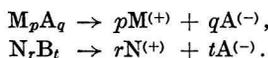
$$\lim_{x_1 \rightarrow 1} \frac{dT_1}{dx_1} = r K_1^{\text{td}}. \quad (9b)$$

By analogy we can write for the second component

$$\lim_{x_2 \rightarrow 1} \frac{dT_2}{dx_2} = p \cdot \frac{R [T_2^f]^2}{\Delta H_2^f} = p K_2^{\text{td}}. \quad (10)$$

2.2. Systems without a common ion

Let us consider the binary system $M_pA_q - N_rB_t$; the components should dissociate completely according to the equations



Let the mole fractions of the substances M_pA_q and N_rB_t be x_1 and x_2 , respectively. Then, according to equation (11) in [1]

$$a_{M_pA_q} = \left[\frac{px_1}{r + x_1(p - r)} \right]^p \cdot \left[\frac{qx_1}{t + x_1(q - t)} \right]^q, \quad (11)$$

$$a_{N_rB_t} = \left[\frac{rx_2}{p + x_2(r - p)} \right]^r \cdot \left[\frac{tx_2}{q + x_2(t - q)} \right]^t. \quad (12)$$

Substituting the activity from the equation (11) derivating the equation (5), into equation (5), and limiting $x_1 \rightarrow 1$, we get

$$\lim_{x_1 \rightarrow 1} \frac{dT_1}{dx_1} = (r + t) \cdot \frac{R [T_1^f]^2}{\Delta H_1^f} = (r + t) \cdot K_1^{\text{td}} \quad (13)$$

and by analogy for the second component

$$\lim_{x_2 \rightarrow 1} \frac{dT_2}{dx_2} = (p + q) \cdot \frac{R [T_2^f]^2}{\Delta H_2^f} = (p + q) \cdot K_2^{\text{td}}. \quad (14)$$

Derivating equation (5) with respect to x_i we get

$$\frac{dT_i}{dx_i} = \frac{R \Delta H_i^f \cdot \frac{1}{a_i} \cdot \frac{da_i}{ax_i}}{(\Delta S_i^f - R \ln a_i)^2}. \quad (15)$$

Limiting equation (15) for $x_i \rightarrow 1$ (when $x_i = a_i$), we obtain

$$\lim_{x_i \rightarrow 1} \frac{dT_i}{dx_i} = \frac{R [T_i^f]^2}{\Delta H_i^f} \cdot \lim_{x_i \rightarrow 1} \frac{da_i}{dx_i} \quad (16)$$

and

$$\lim_{x_i \rightarrow 1} \frac{dT_i}{dx_i} = K_i^{\text{td}} \cdot \lim_{x_i \rightarrow 1} \frac{da_i}{dx_i}. \quad (17)$$

The equation (17) has the general validity: the slope of the tangent to the liquidus curve of the i th component in the point T_i^f is determined by the product of the

constant of thermic depression and of the limiting coefficient of this component. In the special case of an ideal ionic solution, the limiting coefficient is identical with the corresponding Stortebeker correction factor.

In our considerations we assume the activity a_i to be the function of concentration x_i only, and not that of temperature as well. Incorrectness due to this assumption disappears at the limiting transition $x_i \rightarrow 1$.

From this standpoint the equations (9a, 9b), (10), (13), (14), similarly as equations (14) to (17) reported by [1] justify introducing of this empirical Stortebeker factor.

With regard to the definition of cryoscopic constant K_i^{cr} [2, p. 246], we can write

$$K_i^{\text{cr}} = K_i^{\text{td}} \cdot \frac{M_i}{1000}$$

where M_i is the molecular weight of the i th component. The usual expression for temperature drop of primary crystallization of the substance Q , which forms together with the substance Z the solution of the first kind, is as follows

$$\Delta T_Q = K_Q^{\text{cr}} \cdot m_Z = K_Q^{\text{td}} \cdot \frac{M_Q}{1000} m_Z \quad (m_Z \rightarrow 0) \quad (18)$$

(m_Z = molality of the substance Z in the solution $Q-Z$).

When the system $Q-Z$ is an ionic solution, then, in general (for $m_Z \rightarrow 0$) the following holds

$$\Delta T_Q = K_Q^{\text{cr}} \cdot m_Z \cdot k_{Z/Q}^{\text{St}} = K_Q^{\text{cr}} \cdot m_Z \cdot \lim_{x_Q \rightarrow 1} \frac{da_Q}{dx_Q} \quad (19)$$

and

$$\Delta T_Q = K_Q^{\text{td}} \cdot \frac{M_Q}{1000} \cdot m_Z \cdot \lim_{x_Q \rightarrow 1} \frac{da_Q}{dx_Q} \quad (20)$$

3. Determination of the character of liquidus curves in a binary system

3.1. The components form an ideal solution

The character of liquidus curves of simple eutectic systems depends greatly on whether these curves are convex or concave with regard to the concentration axis.

As to the ideal systems, this question has been satisfactorily solved [3, p. 360]; from the equation for the liquidus curve of the i th component it follows that

$$\frac{d^2 T_i}{dx_i^2} = \frac{R \Delta H_i^f (-\Delta S_i^f + R \ln x_i + 2R)}{x_i^2 (\Delta S_i^f - R \ln x_i)^2} \quad (21)$$

From the condition of existence of inflexion point and with regard to the fact that the mole fraction x_i has a physical meaning only in the interval (0; 1), it follows

$$\ln(x_i)_{\text{infl}} = \frac{\Delta S_i}{R} - 2 \quad (22)$$

Substituting in equation (3) for $(x_i)_{\text{infl}}$ from equation (22) we find that

$$(T_i)_{\text{infl}} = \frac{\Delta H_i^f}{2R} \quad (23)$$

and that for the ratio $T_i^f : (T_i)_{\text{infl}}$ it is valid

$$\frac{T_i^f}{(T_i)_{\text{infl}}} = \frac{2R}{\Delta S_i^f} . \quad (24)$$

Since $\ln(x_i)_{\text{infl}} \leq 0$, then

$$\Delta S_i^f \leq 2R . \quad (25)$$

The course of the liquidus curve depends on the fact that, the condition of equation (22) being satisfied, the part of the liquidus curve within the interval $(x_{\text{infl}}, 1)$ is convex with regard to the concentration axis and only the part for $x < x_{\text{infl}}$ becomes concave, supposing, naturally, that there is a real inflexion point on the liquidus curve of the i th substance, *i.e.* that $T_E < T_{\text{infl}}$.

Karapetjan's statement [4, p. 267], that the liquidus curves in ideal binary system can be only concave with regard to the concentration axis x , is evidently erroneous.

3.2. The components form an ideal solution

3.2.1. Systems with a common ion

We consider a binary system $M_p A_q - N_r A_t$ which dissociates completely to ions $M^{(+)}$, $N^{(+)}$, $A^{(-)}$ and $N^{(-)}$. The activities of components are given by equations (6) and (7). Substituting expression (6) in the equation of liquidus curve (5), determining further the second derivative, *i.e.* the expression $d^2 T_1 / dx_1^2$ and putting it equal to zero we get after rearrangement

$$[r + 2(p - r)x_1] \cdot \left[R p \ln \frac{p x_1}{r + (p - r)x_1} - \Delta S_1^f \right] + 2R r p = 0 . \quad (26)$$

This transcendental equation with regard to x_1 has a simple solution for these cases when $p = r$; then we can write

$$\ln(x_1)_{\text{infl}} = \frac{\Delta S_1^f}{R p} - 2 \quad (27)$$

and from the condition that $(x_1)_{\text{infl}} \leq 1$ it follows

$$\Delta S_1^f \leq 2R p . \quad (28)$$

Further it is valid that

$$(T_1)_{\text{infl}} = \frac{\Delta H_1^f}{2R p} , \quad (29)$$

and

$$\frac{T_1^f}{(T_1)_{\text{infl}}} = \frac{2R p}{\Delta S_1^f} . \quad (30)$$

Analogous relations are also valid for the second component.

3.2.2. Systems without a common ion

Activities of components of ideal ionic system M_pA_q and N_rB_t which are completely dissociated to ions $M^{(+)}$, $N^{(+)}$, $A^{(-)}$ and $B^{(-)}$ can be calculated with the aid of equation (11) and (12).

Substituting the equation (11) in (5) and after double derivation we determine from the condition $d^2T_i/dx_i^2 = 0$ under the simplifying assumption that $p = r$ and $q = t$, the following equation

$$2R(p + q) - \Delta S_1^f + (p + q) R \ln(x_1)_{\text{infl}} = 0.$$

Then we find that

$$\ln(x_1)_{\text{infl}} = \frac{\Delta S_1^f}{R(p + q)} - 2. \quad (31)$$

From the condition that $(x_1)_{\text{infl}} \leq 1$ it follows

$$\Delta S_1^f \leq 2R(p + q). \quad (32)$$

Further we find that

$$(T_1)_{\text{infl}} = \frac{\Delta H_1^f}{2R(p + q)} \quad (33)$$

and

$$\frac{T_1}{(T_1)_{\text{infl}}} = \frac{2R(p + q)}{\Delta S_1^f}. \quad (34)$$

Analogous relations are valid for the second component.

4. Discussion of the character of liquidus curves in binary systems

Convex parts (with regard to the concentration axis) and the existence of inflexion point on the liquidus curves of components of a system constitute their characteristic features. A necessary and sufficient condition for occurrence of a convex part, supposing the system behaves as an ideal system, is the relation

$$\Delta S_i^f \leq 2R. \quad (35)$$

When, moreover

$$T_{\text{infl}} > T_E$$

where T_E is temperature of the eutectic point in the given system, then real inflexion point occurs on the liquidus curve and the convex course of the liquidus curve changes and becomes concave. Most alkali metals and alkali earth metals do not satisfy the condition of equation (35). Thus, e.g., the values of ΔS_i^f for all alkali metal halides range from 4.72 to 6.27 cal deg⁻¹ mole⁻¹ ([5] p. 184). Substances which occur as additives or admixtures in the aluminium electrolytes have ΔS_i^f greater than $2R$; thus, e.g. $\Delta S_{\text{CaF}_2}^f = 4.3$ cal deg⁻¹ mole⁻¹, as reported by Delbove [6], and 5.8 according to Rogers *et al.* [7], $\Delta S_{\text{MgF}_2}^f = 9.0$ [8], $\Delta S_{\text{Na}_2\text{SO}_4}^f = 4.9$ [5] *etc.* Very high values of ΔS_i^f are reported for both cryolites, $\Delta S_{\text{Li}_3\text{AlF}_6}^f = 19.4$ [9], $\Delta S_{\text{Na}_3\text{AlF}_6}^f = 20.9$ [10]. This explains why on the phase diagram of these substances with

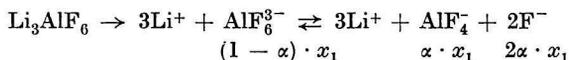
substances which have only one non-common ion, as far as they behave at least approximately as ideal, the convex shape does not exist.

The situation is altogether different when there are substances which have two or more kinds of different ions. Let us consider a system M_2A-N_2A . Then, according to equation (28), a convex part of the liquidus curve can exist only when the following inequality is satisfied

$$\Delta S_i^f \leq 2R p = 4R$$

and this condition is satisfied by most inorganic substances (by all above mentioned substances, except Li_3AlF_6 and Na_3AlF_6). Thus it is obvious that for p (or k_{ij}^{st}) > 2 the condition for the existence of an inflexion point will be satisfied, too.

Let us consider the liquidus curve of MgF_2 in the simple eutectic system $Li_3AlF_6-MgF_2$. If Li_3AlF_6 would form non-dissociated molecules only, then no inflexion points would occur on the liquidus curve of MgF_2 . However, it is well-known that Li_3AlF_6 dissociates in these conditions most probably according to the following scheme



where α is the degree of dissociation of AlF_6^{3-} , $0 < \alpha < 1$,

x_1 is the mole fraction of the lithium cryolite Li_3AlF_6 in the system under consideration.

Thus one molecule Li_3AlF_6 brings together four new particles into the molten MgF_2 (i.e. three ions Li^+ , $(1 - \alpha) \cdot AlF_6^{3-}$ and $\alpha \cdot AlF_4^-$), then

$$\Delta S_{MgF_2}^f = 9 \text{ cal deg}^{-1} \text{ mole}^{-1} < 8R \cong 16 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

the condition for the existence of the inflexion point is satisfied and hence on the liquidus curve of MgF_2 in the system $Li_3AlF_6-MgF_2$ an inflexion point appears [11]. This confirms at least the qualitative correctness and applicability of the model of ideal ionic solutions even when x_i differs considerably from 1.

References

1. Malinovský M., *Chem. Zvesti* **23**, 801 (1969).
2. Hála E., Reiser A., *Fyzikální chemie I*. Publishing House of the Czechoslovak Academy of Sciences, Prague, 1960.
3. Prigogine I., Defay R., *Chemische Thermodynamik*. VEB Deutscher Verlag f. Grundstoffindustrie, Leipzig, 1962.
4. Karapetjanc M. Ch., *Chimičeskaja termodinamika*, 2nd Ed. Goschimizdat, Moscow, 1953.
5. Janz G. J., *Molten Salts Handbook*. Academic Press, New York, 1967.
6. Delbove Fr., *C. R. Acad. Sci. (Paris)* **252**, 2192 (1961).
7. Rogers P. S., Tomlison J. W., Richardson F. D., *Met. Soc. Conf.* **8**, 909 (1961).
8. Gluško V. P. (Ed.), *Termodinamičeskije svojstva individualnych veščestv II*. Izdatelstvo Akademii Nauk SSSR, Moscow, 1962.
9. Malinovský M., *Chem. Zvesti* **21**, 783 (1967).
10. Frank W. B., *J. Phys. Chem.* **65**, 2081 (1961).
11. Kašíková S., Malinovský M., *Chem. Zvesti*, in press.

Translated by V. Šašková