Liquidus Curves of Ideal Ionic Systems. I.

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The Temkin model of ideal (perfect) ionic solution is discussed. General relations for calculation of activities of individual components of ideal ionic solution have been derived. The dependence $a_i = f(x_i)$ for the components of binary systems is analyzed both in the case when two substances contain identical kind of ions ("common ions") and when there are not identical ions in these substances. The concept of the limiting coefficient is introduced. The numerical value of this coefficient is identical with the Stortenbeker correction factor in the equation which describes the temperature drop of (primary) crystallization of the pure component from the solution of the given composition.

Although equations describing liquidus curves of components of ideal systems have been formulated long ago [1-3], hardly any attention was paid to problems of liquidus curves of components of solutions which consisted solely of ions. The first paper dealing with this problem was published in 1938 by *Herasymenko* [4]. Nevertheless, the paper by *Temkin* [5] aroused greatest interest since in it criteria for ideal (perfect) ionic solution were formulated and the author established the dependence of activities of constituents of the solution on concentration expressed in the so-called ionic fractions. He used for this purpose the ternary reciprocal system Ca²⁺, Fe²⁺//O²⁻, S²⁻. But he neither did show the possibility of using the relation $a_i = f(a_i)$ for cryoscopic investigation of systems, nor did he analyze the rules which determine the course of the liquidus curves of the constituents of those systems which behave like ideal ionic solutions.

The concept of ideal ionic solution found its successful application in the special field of calculation of the liquidus curve of primary crystallization of ionic constituents in different systems, while the dependence of their activities on concentration is expressed according to Temkin's suggestions. *Voskresenskaja* and *Frohberg* [6, 7] - and partly also *Babuškin et al.* [8] deal with these problems in their papers, though, no principally new ideas can be found in their publications. We even find sometimes an incorrect determination of the relationship $a_i = f(w_i)$ [9]. Since the model of ideal ionic solution is being often applied to different categories of molten systems [10-15], we find it advisable to discuss these problems in details.

1. Establishing of general equations for calculation of the activities of constituents of ideal ionic solutions

The Temkin model is based on following assumptions:

I. The liquid solution and its components as well consist solely of ions (simple or complex). Electrically neutral particles (e.g. molecules), are not present.

II. Since in the investigated solution the concentration of electrically charged ions is relatively high, considerable forces of electrostatic character arise there. Consequently, the structure of the liquid solution resembles that of the solid crystal, *i.e.* each ion is surrounded by ions of opposite polarity.

This, however, rules out the exchange a cation for an anion in its position and *vice versa*. The solution as a whole can be considered as if consisting of two different, though inseparable solutions of cations and anions. Consequently each ion can change position within its "own" solution only.

III. Within their own solutions all ions are equivalent, disregarding the magnitude of their electrical charge. For this reason their statistical distribution can take place without any limitations.

Hence it follows that:

A. The enthalpies of mixing of the cationic as well as of anionic solutions are zero, *i.e.* $\Delta H_{\rm mix}^{(+)} = 0$, $\Delta H_{\rm mix}^{(-)} = 0$ and consequently the enthalpy of mixing of the whole solution $\Delta H_{\rm mix} = 0$.

B. The entropies of mixing of the cationic and anionic solution $\Delta S_{\text{mix}}^{(+)}$, $\Delta S_{\text{mix}}^{(-)}$, have solely a configurative character.

This means that in the equation

$$\Delta G_{\rm mix} = \Delta H_{\rm mix} - T \,\Delta S_{\rm mix} \tag{1}$$

only the correction of the term $T \Delta S_{\min x}$, comparing with the value in an ideal nonionic solution, takes place. The term $\Delta H_{\min x}$ is supposed to be zero as in the case of an ideal non-ionic solution.

Let us consider a system in which there are the constituents M_pA_q , N_rB_t , M_sB_v and N_eA_d (M⁽⁺⁾, N⁽⁺⁾ are cations, A⁽⁻⁾, B⁽⁻⁾ are anions, the magnitude of electrical charge is irrelevant).

These constituents dissociate according to the schemes

$$\begin{split} \mathbf{M}_{p}\mathbf{A}_{q} &\to p\mathbf{M}^{(+)} + q\mathbf{A}^{(-)}, \\ \mathbf{N}_{r}\mathbf{B}_{t} &\to r\mathbf{N}^{(+)} + t\mathbf{B}^{(-)}, \\ \mathbf{M}_{s}\mathbf{B}_{v} &\to s\mathbf{M}^{(+)} + v\mathbf{B}^{(-)}, \\ \mathbf{N}_{e}\mathbf{A}_{d} &\to e\mathbf{N}^{(+)} + d\mathbf{A}^{(-)}. \end{split}$$

Let us assume that a system consisting of these substances contains solely ions formed according to the above equations. Let the number of moles of the first, second, third and fourth substance be n_1 , n_2 , n_3 , and n_4 , respectively. Then $(n_1 + n_2 + n_3 + n_4)$ moles of mixture of these four substances will contain

$$(n_1p + n_3s) \text{ moles } \mathbf{M}^{(+)},$$

 $(n_2r + n_4e) \text{ moles } \mathbf{N}^{(+)},$
 $(n_1q + n_4d) \text{ moles } \mathbf{A}^{(-)},$
 $(n_2t + n_3v) \text{ moles } \mathbf{B}^{(-)}.$

The number of possibilities P_{I} for the realization of the state of liquid phase consisting solely of cations $M^{(+)}$ or of cations $N^{(+)}$ can be expressed by equations

$$P_{\rm I}[{
m M}^{(+)}] = 1; \quad P_{\rm I}[{
m N}^{(+)}] = 1.$$

For the number of possibilities to form a common solution of cations from these two pure phases the following is valid LIQUIDUS CURVES OF IDEAL IONIC SYSTEMS. I

$$P_{II}^{(+)} = \frac{[N(n_1p + n_3s + n_2r + n_4e)]!}{[N(n_1p + n_3s)]! [N(n_2r + n_4e)]!},$$
(2)

where N is the Avogadro number.

The thermodynamic probability of the formation of cationic solution $W_{\text{mix}}^{(+)}$ from phases constituted by cations $M^{(+)}$ and $N^{(+)}$ is expressed by the equation

$$W_{\rm mix}^{(+)} = \frac{P_{\rm II}^{(+)}}{P_{\rm I}[{\rm M}^{(+)}] \cdot P_{\rm I}[{\rm N}^{(+)}]} = P_{\rm II}^{(+)} \,. \tag{3}$$

By analogy, for thermodynamic probability of formation of anionic solution $W_{\text{mix}}^{(-)}$ from pure phases constituted by anions $A^{(-)}$ and $B^{(-)}$ we can write

$$W_{\rm mix}^{(-)} = \frac{[N(n_1q + n_4d + n_2t + n_3v)]!}{[N(n_1q + n_4d)]! [N(n_2t + n_3v)]!} \,. \tag{4}$$

The expressions for $W_{\text{mix}}^{(+)}$, $W_{\text{mix}}^{(-)}$ can be simplified using the Stirling formula. We obtain

$$\ln W_{\min}^{(+)} = -N[n_1 \cdot \ln x_{\mathbf{M}^{(+)}}^p + n_3 \cdot \ln x_{\mathbf{M}^{(+)}}^s + n_2 \cdot \ln x_{\mathbf{N}^{(+)}}^r + n_4 \cdot \ln x_{\mathbf{N}^{(+)}}^e], \qquad (5)$$

$$\ln W_{\min}^{(-)} = -N[n_1 \cdot \ln x_{A^{(-)}}^q + n_4 \cdot \ln x_{A^{(-)}}^d + n_2 \cdot \ln x_{B^{(-)}}^t + n_3 \cdot \ln x_{B^{(-)}}^v].$$
(6)

Using the Boltzmann formula $S = \mathbf{k} \cdot \ln W$, we get for the entropy of mixing of the whole solution

$$\Delta S_{\mathrm{mix}} = \Delta S_{\mathrm{mix}}^{(+)} + \Delta S_{\mathrm{mix}}^{(-)} = oldsymbol{k} [\ln W_{\mathrm{mix}}^{(+)} + \ln W_{\mathrm{mix}}^{(-)}]$$

and substituting from eq. (5) and (6) we have

$$egin{aligned} & \varDelta S_{ ext{mix}} = - \pmb{R} [n_1 \cdot \ln x^p_{ ext{M}^{(+)}} \cdot x^q_{ ext{A}^{(-)}} + n_2 \cdot \ln x^r_{ ext{N}^{(+)}} \cdot x^t_{ ext{B}^{(-)}} + \ & + n_3 \cdot \ln x^s_{ ext{M}^{(+)}} \cdot x^r_{ ext{B}^{(-)}} + n_4 \cdot \ln x^e_{ ext{N}^{(+)}} \cdot x^d_{ ext{A}^{(-)}}] \,. \end{aligned}$$

Then we have for the free enthalpy of the solution G_{II}

$$G_{\rm II} = n_1 H_1^0 + n_2 H_2^0 + n_3 H_3^0 + n_4 H_4^0 - n_1 T S_1^0 - n_2 T S_2^0 - n_3 T S_3^0 - n_4 T S_4^0 + RT[n_1 \cdot \ln x_{\rm M^{(+)}}^p \cdot x_{\rm A^{(-)}}^q + n_2 \cdot \ln x_{\rm N^{(+)}}^r \cdot x_{\rm B^{(-)}}^t + n_3 \cdot \ln x_{\rm M^{(+)}}^s \cdot x_{\rm B^{(-)}}^v + n_4 \cdot \ln x_{\rm N^{(+)}}^e \cdot x_{\rm A^{(-)}}^d]$$
(7)

and hence the chemical potentials μ_i of individual substances are

$$\begin{split} \mu_{1} &= \frac{\partial G_{II}}{\partial n_{1}} = \mu_{1}^{0} + \boldsymbol{R}T \cdot \ln x_{M^{(+)}}^{p} \cdot x_{A^{(-)}}^{q}, \\ \mu_{2} &= \frac{\partial G_{II}}{\partial n_{2}} = \mu_{2}^{0} + \boldsymbol{R}T \cdot \ln x_{N^{(+)}}^{r} \cdot x_{B^{(-)}}^{l}, \\ \mu_{3} &= \frac{\partial G_{II}}{\partial n_{3}} = \mu_{3}^{0} + \boldsymbol{R}T \cdot \ln x_{M^{(+)}}^{s} \cdot x_{B^{(-)}}^{p}, \\ \mu_{4} &= \frac{\partial G_{II}}{\partial n_{4}} = \mu_{4}^{0} + \boldsymbol{R}T \cdot \ln x_{N^{(+)}}^{s} \cdot x_{A^{(-)}}^{d}. \end{split}$$

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Comparing with the relation $\mu_i = \mu_i^0 + \mathbf{R}T \cdot \ln a_i$ we obtain

$$a_{M_pA_q} = x_{M^{(+)}}^p \cdot x_{A^{(-)}}^q, \qquad (8a)$$

$$a_{\mathbf{N}_{\mathbf{r}}\mathbf{B}_{t}} = x_{\mathbf{N}^{(+)}}^{\mathbf{r}} \cdot x_{\mathbf{B}^{(-)}}^{t}, \qquad (8b)$$

$$a_{M,B_{v}} = x_{M^{(+)}}^{s} \cdot x_{B^{(-)}}^{v}, \qquad (8c)$$

$$a_{\mathbf{N}_{e}\mathbf{A}_{d}} = x_{\mathbf{N}^{(-)}}^{e} \cdot x_{\mathbf{A}^{(-)}}^{d}, \qquad (8d)$$

where the symbols $x_{\rm M}^{(+)}$, $x_{\rm N}^{(+)}$, $x_{\rm A}^{(-)}$, $x_{\rm B}^{(-)}$ designate the ionic fractions of the respective kind of ions in the system under consideration.

By the above procedure we get equations for the activities of all four constituents of the ternary reciprocal system

$$M^{(+)}, N^{(+)}//A^{(-)}, B^{(-)}.$$

In case when the expression $a_i = f(x_i)$ should be used in the equation for calculation of the liquidus curves of the given substance in a binary system, it suffices to consider the formation of the solution of such two substances which form together a simple eutectic system; the calculation procedure is identical.

2. General rules concerning the dependence $a_i = f(x_i)$

2.1. Systems with one common ion

Let us consider the binary system $M_pA_q - N_rA_t$ whose components dissociate according to the schemes

$$\mathrm{M}_{p}\mathrm{A}_{q} \rightarrow p\mathrm{M}^{(+)} + q\mathrm{A}^{(-)},$$

 $\mathrm{N}_{r}\mathrm{A}_{t} \rightarrow r\mathrm{N}^{(+)} + t\mathrm{A}^{(-)}.$

Let the mole fraction of the substance M_pA_q in this system be x_1 and the mole fraction of the substance N_rA_t let be x_2 .

According to equation (8a) the following is valid for the activity of the first of these components

$$a_{\mathrm{M}_{p}\mathrm{A}_{q}} = x_{\mathrm{M}^{(+)}}^{p} \cdot x_{\mathrm{A}^{(-)}}^{q} = \left[\frac{px_{1}}{px_{1} + rx_{2}} \right]^{p} \cdot \left[\frac{qx_{1} + tx_{2}}{qx_{1} + tx_{2}} \right]^{q}.$$

Since $x_1 + x_2 = 1$

$$a_{M_{p}A_{q}} = \left[\frac{px_{1}}{px_{1} + r(1 - x_{1})}\right]^{p} = \left[\frac{px_{1}}{r + (p - r)x_{1}}\right]^{p}.$$
(9)

For $a_{N_rA_t}$ we obtain

$$a_{N-A_{t}} = \left[\frac{rx_{2}}{p + (r - p)x_{2}}\right]^{r}.$$
 (10)

From the equations (9) and (10) it follows that in systems with a common ion the activity equals directly the mole fraction only when p = r = 1; then

$$a_{\mathbf{M}_{p}\mathbf{A}_{q}} = x_{1}; \quad a_{\mathbf{N}_{r}\mathbf{A}_{t}} = x_{2}.$$

The value of coefficients of the common ion (i.e. q or t), is irrelevant.

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When p = r (p, r are evidently integers), then

$$a_{\mathbf{M}_{p}\mathbf{A}_{q}} = x_{1}^{p}; \quad a_{\mathbf{N}_{r}\mathbf{A}_{t}} = x_{2}^{r} = x_{2}^{p}.$$

The values of the coefficients q and t are irrelevant.

2.2. Systems without common ion

We consider the binary system $M_pA_q - N_rB_t$. We assume the complete dissociation of components according to the schemes

$$M_p A_q \rightarrow p M^{(+)} + q A^{(-)},$$

 $N_r B_t \rightarrow r N^{(+)} + t B^{(-)}.$

Let the mole fractions of the substances M_pA_q and N_rB_t be x_1 and x_2 , respectively. Then

$$a_{\mathbf{M}_{p}\mathbf{A}_{q}}=x_{\mathbf{M}^{(+)}}^{p}\cdot x_{\mathbf{A}^{(-)}}^{q}=\left[rac{px_{1}}{px_{1}+rx_{2}}
ight]^{p}\cdot \ \left[rac{qx_{1}}{qx_{1}+tx_{2}}
ight]^{q}$$

or eliminating x_2

$$a_{\mathbf{M}_{\mathbf{p}}\mathbf{A}_{\mathbf{q}}} = \left[\frac{px_1}{r + x_1(p - r)}\right]^p \cdot \left[\frac{qx_1}{t + x_1(q - t)}\right]^q.$$
(11)

By analogy we find that

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

In some special cases these relationships can be simplified. Thus, e.g., when p = q = r = t = 1 (*i.e.* when we have the system MA-NB)

$$a_{
m MA} = x_1^2; \;\; a_{
m NB} = x_2^2.$$

When p = r = 1, q = t = 2 (*i.e.* in the system MA₂-NB₂) or p = r = 2, q = t = 1 (*i.e.* in the system M₂A-N₂B)

$$a_{{
m MA}_2}=a_{{
m M}_2{
m A}}=x_1^3; \ \ a_{{
m NB}_2}=a_{{
m N}_2{
m B}}=x_2^3.$$

When p = r, q = t, then

$$a_{{
m M}_{p}{
m A}_{q}}=x_{1}^{p+q}; \ \ a_{{
m N}_{p}{
m B}_{q}}=x_{2}^{p+q}$$

3. The limiting coefficient

For any ideal solution over the whole range of concentration and at all temperatures and pressures we have $a_i = x_i$ [16, p. 253], where a_i is the activity of the *i*th substance in the given solution. For standard state we take the state of pure *i*th substance at the same temperature and in the same state as the solution under investigation, *i.e.* $a_i = x_i$ when $x_i = 1$. We assume that our system is under a constant pressure which is greater than the vapour pressure within the considered temperature interval. In case of non-ideal solution, in general it is valid that $x_i \neq 1$, $a_i \neq x_i$. When x_i approaches the value of unity, then the difference between a_i and x_i diminishes constantly. Frohberg [7] called them the solutions of , the first kind". The approaching of values a_i and x_i for x_i near to unity means that the linear dependence $x_i = f(x_i)$, and the dependence $a_1 = f(x_i)$ (in general case a non-linear dependence), practically coincide at a sufficiently high value of x_i , or, at least they have a common tangent for $x_i \to 1$. These relations can be simply expressed

$$\lim_{x_i \to 1} \frac{\mathrm{d}a_i}{\mathrm{d}x_i} = 1. \tag{13}$$

We shall call the term on the left-hand side of the equation (13), the *limiting* coefficient of ith substance".

For an ideal solution the value of the ratio da_i/dx_i naturally equals unity at all values of x_i , T and P, and consequently, the equation (13) is also valid for the ideal solution. Hence it is typical for solutions of the first kind, ideal or non-ideal, that they satisfy the equation (13).

In case of ionic solutions of fused electrolytes we have, however, a quite different situation. Thus, e.g., in binary systems of the type $M_pA_q - N_rA_t$ with a common ion, we find by derivation of the equations (9) and (10) with respect to x_1 and x_2 , respectively, and by setting $x_1(x_2) = 1$, that the limiting coefficients are for M_pA_q :

$$\lim_{x_1 \to 1} \frac{\mathrm{d}a_1}{\mathrm{d}x_1} = r; \tag{14}$$

for
$$N_r A_t$$
:

$$\lim_{x_2 \to 1} \frac{\mathrm{d}a_2}{\mathrm{d}x_2} = p \,. \tag{15}$$

In binary systems of the type $M_pA_q - N_rB_t$ we find by analogy that for M_pA_q :

$$\lim_{x_1 \to 1} \frac{\mathrm{d}a_1}{\mathrm{d}x_1} = r + t; \tag{16}$$

for N_rB_t:

$$\lim_{x_2 \to 1} \frac{\mathrm{d}a_2}{\mathrm{d}x_2} = p + q. \tag{17}$$

In Fig. 1 we see the course of the function $a_i = f(x_i)$ for an ideal solution, for a non-ideal solution of the first kind and for an ideal solution of the second kind (for the component NB in the system $M_3A - NB$). The tangent to the curve $a_{NB} = f(x_{NB})$ for $x_{NB} = 1$ is also shown. For the slope of this tangent it holds that

$$k = \lim_{x_{\rm NB} \to 1} \frac{\mathrm{d}a_{\rm NB}}{\mathrm{d}x_{\rm NB}} = 4.$$



Fig. 1. The course of the function $a_i = f(x_i)$.

1. relationship $a_i = x_i$ for ideal solution; 2. relationship $a_i = f(x_i)$ for non-ideal solution of the first kind; 3. relationship $a_i = f(x_i)$ for ideal solution of the second kind, $x_i = x_{\rm NB}$ in the system M₃A-NB; 4. slope of the tangent to the curve $a_{\rm NB} = f(x_{\rm NB})$ in the system M₃A-NB at $x_{\rm NB} \rightarrow 1$.

In general the following is valid for the solutions of fused electrolytes

$$\lim_{x_i \to 1} \frac{\mathrm{d}a_i}{\mathrm{d}x_i} \neq 1.$$
⁽¹⁸⁾

This inequality is typical for the given category of solutions. Frohberg stressed [7] that they did not obey the Raoult and Henry laws and for this reason he called them solutions ,,of the second kind".

From the equations (14) and (17) it follows that in individual cases the values of limiting coefficients are numerically equal to the number of new (foreign) particles, which, in the course of the above described dissociation, have been introduced into the system (e.g. the substance M_pA_q), by one molecule of the substance N_rA_t or N_rB_t or, more general, the number of new particles which appear in the system of pure M_pA_q due to introducing of one molecule of the substance N_rA_t or N_rB_t . Consequently the limiting coefficients are identical with the Stortenbeker correction factors k^{St} . These factors [17] are used in equations for calculation of temperature decrease of the primary crystallization of the substance Q(Z) achieved by the addition of substance Z(Q), when substances Q and Z are electrolytes:

$$\Delta T_Q = K_Q^{\rm cr} \cdot m_Z \cdot k_{Z/Q}^{\rm St} \tag{19}$$

where ΔT_Q is the temperature decrease of primary crystallization of the substance Q, K_Q^{cr} is the cryoscopic constant of the substance Q,

- m_Z is the molal concentration of the substance Z in the system Q-Z,
- $k_{Z/Q}^{\text{St}}$ is the Stortenbeker correction factor for the substance Z with regard to the system Q-Z.

Then in the system Q-Z it is

$$\lim_{x_Q \to 1} \frac{\mathrm{d}a_Q}{\mathrm{d}x_Q} = k_{Z/Q}^{\mathrm{St}} \tag{20}$$

and

$$\lim_{x_z \to 1} \frac{\mathrm{d}a_z}{\mathrm{d}x_z} = k_{Q/Z}^{\mathrm{St}} \,. \tag{21}$$

With the aid of the model of ideal ionic solutions the Stortenbeker correction factors can be easily derived.

Finally we want to point out that when $a_i = x_i$, then the limiting coefficient equals one. When, on the other hand, $a_i \neq x_i$ ($x_i < 1$), the limiting coefficient mostly differs from one, but in some cases it can equal one.

Thus, e.g., in the systems of the type $MA - N_rA$

$$a_{N_rA} = a_2 = \left[rac{rx_2}{1 + x_2(r-1)}
ight]^r
eq x_2 \quad (0 < x_2 < 1)$$

but

$$\lim_{x_2 \to 1} \frac{\mathrm{d}a_2}{\mathrm{d}x_2} = 1$$

This is in accord with the fact that one molecule of the substance MA introduces only one new particle, *i.e.* the ion $M^{(+)}$ into the fused N_rA .

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