

Universal relationship for the activity of the i -th component in binary systems*

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The activity of the i -th component in the binary system " i - j " may be advantageously defined as $a_i = x_i^{k_{ji}}$, where the coefficient k_{ji} characterizes the interaction of the two components. For $x_i \rightarrow 1$ this coefficient is identical with the Stortenbeker correction factor. The suggested definition of the activity provides a rational explanation of the magnitude of the slope of tangent to the liquidus curve in the melting point of the i -th substance and besides it covers a wider field of application than some other relations used for the dependence $a_i = f(x_i)$.

Let us consider the equilibrium "solidus-liquidus" in a simple eutectic system formed by the components " i " and " j ". Classical thermodynamic analysis gives for the dependence $T_i = f(a_i)$ the relation

$$T_i = \frac{\Delta H_i^f}{\Delta S_i^f - R \ln a_i}, \quad (1)$$

where T_i — crystallization temperature of the i -th substance of the mixture,
 ΔH_i^f — melting enthalpy of the i -th component,
 ΔS_i^f — melting entropy of the i -th component,
 a_i — activity of the i -th component in the given mixture.

Relation (1) holds on the assumption that the change of the molar heat capacity in the "solidus-liquidus" process, $\Delta C_p^{l/s}$, is equal to zero [1], or if the considered temperature interval $T_i^f - T_i$ (T_i^f is the melting point of the pure i -th component) is small enough.

The experimental study of the phase equilibria in the systems under consideration leads to the dependence $T_i = f(x_i)$, where x_i is the mole fraction of the i -th substance in a liquid solution. In order to confront experimental and theoretical data calculated using eqn (1), it is necessary to know the function dependence $a_i = f(x_i)$. Classical thermodynamics cannot provide the concrete form of this dependence. For this purpose it is necessary to apply either the relation following from a certain model or an empirical or semiempirical dependence, which has to satisfy some physical boundary conditions.

In the study of molten systems formed by ions, mostly relation following from the Temkin model of ideal ionic solutions [2] is used. Its application, however, has been found in some cases to encounter with complications. If the components introduce

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a greater number of different ions into a melt, then the relations for the calculation of the activity are comparably complicated.

A special kind of difficulty occurs if one of the components is formed by cryolites. These substances dissociate especially at low concentrations by several schemes to yield different types of ions. Thus, *e.g.* in the system NaCl—Na₃AlF₆ the number of non-common ions brought in by Na₃AlF₆ into NaCl increases formally from 1.7 (at the eutectic point of the system, *i.e.* 11.0 mole % Na₃AlF₆) up to 7 (for zero concentration of Na₃AlF₆). At the eutectic concentration the equilibrium $\text{AlF}_6^{3-} \rightleftharpoons \text{AlF}_4^- + 2\text{F}^-$ is assumed, for the concentration of Na₃AlF₆ lower than 1.2 mole % the supposed equilibrium is $\text{AlF}_4^- + 2\text{Cl}^- \rightleftharpoons \text{AlF}_2\text{Cl}_2 + 2\text{F}^-$ and for quite low concentrations it is $\text{AlF}_2\text{Cl}_2 + 2\text{Cl}^- \rightleftharpoons \text{AlCl}_4^- + 2\text{F}^-$ [3]. Each of these dissociation schemes leads to a different expression for the activity of NaCl and Na₃AlF₆, respectively. Thus, to express the dependence of the activity of NaCl on its concentration along the liquidus curve of NaCl in the concentration range of 100—89 mole % NaCl, as much as three different relations are needed. In addition we must be aware of the fact that the Temkin model is in principle inapplicable if, besides the ions, also the particles of molecular dimension but without any electric charge are present in the solution.

All these defects can be removed by using the relationship

$$a_i = x_i^{k_{ji}}, \quad (2)$$

where k_{ji} is a certain coefficient*, which is a function of the nature of both the substances forming the binary system as well as of the concentration. Let us call this dependence the "universal relationship". Apparently it follows from eqn (2):

$$\lim_{x_i \rightarrow 1} \ln a_i = 1.$$

Thus, like for the Temkin model, the standard state for the universal relationship is the pure (in most cases undercooled) liquid state of the *i*-th substance at the temperature and pressure of the system.

A. Rational deduction of the universal relationship

The equation for the liquidus curve of an ideal solution

$$T_i = \frac{\Delta H_i^f}{\Delta S_i^f - R \ln x_i} \quad (3)$$

derived with respect to x_i yields the relation

$$\frac{dT_i}{dx_i} = \frac{R \Delta H_i^f}{(\Delta S_i^f - R \ln x_i)^2} \cdot \frac{1}{x_i}. \quad (4)$$

(Both ΔH_i^f and ΔS_i^f are assumed to be constant.)

Experimentally it has been found, however, that in general the right side of eqn (4) has to be corrected by multiplication by the coefficient k_{ji} , which is a function of the dissociation nature of both components *i* and *j*, and also — in general case — of the concentration.

* Note: The present paper being in press, a paper by P. Fellner and J. Majling was published: *Chem. Zvesti* 27, 728 (1973), in which for the computation of the course of liquidus curves the relation was used $a = x^k$ (k being an integer identical with the Stortenbeker correction factor).

$$\frac{dT_i}{dx_i} = \frac{R \Delta H_i^f}{(\Delta S_i^f - R \ln x_i)^2} \cdot \frac{1}{x_i} \cdot k_{j/i}. \quad (5)$$

The equation of the liquidus curve of a real solution (eqn (1)) derived with respect to x_i leads to the relation

$$\frac{dT_i}{dx_i} = \frac{R \Delta H_i^f}{(\Delta S_i^f - R \ln a_i)^2} \cdot \frac{1}{a_i} \cdot \frac{da_i}{dx_i}. \quad (6)$$

Assumption that a_i is a function of x_i only is for a not too wide temperature interval satisfactorily fulfilled. Then also the dependence of $k_{j/i}$ on the concentration may be neglected. It holds that in the same interval $\ln a_i \approx \ln x_i$. Then comparing eqns (5) and (6) we obtain

$$\frac{1}{a_i} \cdot \frac{da_i}{dx_i} = \frac{1}{x_i} \cdot k_{j/i} \quad (7)$$

and by separation of the variables and integration we will have

$$\ln a_i = k_{j/i} \cdot \ln x_i + \ln C$$

and

$$a_i = x_i^{k_{j/i}} + C, \quad (8)$$

respectively.

The value of the integration constant C may be easily determined in the following way: if $x_i = 1$, then also $a_i = 1$ and thus $C = 0$.

Therefore it definitely holds that

$$a_i = x_i^{k_{j/i}}. \quad (9)$$

B. The ideal case: $k_{j/i} = \text{const}$

Let us assume that regardless of the value x_i the relation $k_{j/i} = \text{const} = k_{j/i}^{\text{St}}$ holds. Then for the liquidus temperature of the i -th component of such a solution we obtain eqn

$$T_i = \frac{\Delta H_i^f}{\Delta S_i^f - R k_{j/i}^{\text{St}} \ln x_i}. \quad (10)$$

It follows from eqn (10) that for the special case, if $k_{j/i}^{\text{St}} = 0$ the activity cannot be defined using eqn (2). This limitation is, however, not very important, since the systems of that kind only seldom occur (those of the type MF—M₃AlF₆ belong to them).

From eqn (2) we obtain for $k_{j/i} = \text{const}$

$$\frac{da_i}{dx_i} = k_{j/i} \cdot x_i^{k_{j/i}-1} \quad (11)$$

and

$$\lim_{x_i \rightarrow 1} \frac{da_i}{dx_i} = k_{j/i}^0 = k_{j/i}^{\text{St}} = \text{const}. \quad (12)$$

Consequently the limiting coefficient that we denoted as $k_{j/i}^0$ is identical with the Storbekker correction factor $k_{j/i}^{\text{St}}$ [4, 5].

Thus it holds in general

$$\lim_{x_i \rightarrow 1} k_{ji} = k_{ji}^{\text{St}}. \quad (13)$$

For the slope of tangent to the liquidus curve of the i -th component we obtain from eqn (10) the relation (5).

With respect to eqns (11) and (13) eqn (14) is valid:

$$\lim_{x_i \rightarrow 1} \frac{dT_i}{dx_i} = \frac{R(T_i^f)^2}{\Delta H_i^f} k_{ji}^{\text{St}} = K_i^{\text{td}} \cdot k_{ji}^{\text{St}}, \quad (14)$$

where K_i^{td} is the constant of thermal depression of the i -th substance [4, 5].

Thus eqn (14) yields the value of the slope of tangent to the liquidus curve of the i -th component at a temperature unlimitedly approaching T_i^f . It has to be pointed out that eqn (14) also holds for the case when $\Delta C_p^{l/s} \neq 0$, since the corrections caused by this simplification are annulated at $x_i \rightarrow 1$. In the same way also the physical condition of the existence of the inflection point (real or irrational) [4, 5] on the liquidus curve of the i -th component can be easily determined. The well-known mathematical condition $d^2T_i/dx_i^2 = 0$ gives after some rearrangement

$$\ln x_i(\text{infl}) = \frac{\Delta S_i^f}{R \cdot k_{ji}^{\text{St}}} - 2. \quad (15)$$

Since $x_i \rightarrow 1$, $\ln x_i \leq 0$, this leads to the following physical condition of the occurrence of an inflection point on the liquidus curve of the i -th component in the range of the values of x_i ($0; 1$):

$$\Delta S_i^f \leq 2R \cdot k_{ji}^{\text{St}}. \quad (16)$$

For higher values of k_{ji}^{St} the probability of the occurrence of an inflection point considerably increases.

Relations (15) and (16) exactly hold only if $\Delta C_p^{l/s} = 0$. However, even if this condition is not fulfilled, they still yield qualitatively correct results.

C. The general case: $k_{ji} \neq \text{const}$

Thus we may define the activity as

$$a_i = x_i^{f(x_i)} = e^{f(x_i) \ln x_i} \quad (17)$$

or

$$a_i = x_i^{k_{ji}^{\text{St}} \cdot \gamma_i}. \quad (18)$$

It apparently must hold in the first case that $\lim_{x_i \rightarrow 1} f(x_i) \ln x_i = 0$ for $x_i \rightarrow 1$.

Further we find that

$$\frac{da_i}{dx_i} = e^{f(x_i) \ln x_i} \cdot \left[f'(x_i) \ln x_i + \frac{1}{x_i} f(x_i) \right]$$

and from there

$$\lim_{x_i \rightarrow 1} \frac{da_i}{dx_i} = \lim_{x_i \rightarrow 1} \frac{1}{x_i} f(x_i) = k_{ji}^{\text{St}}.$$

Therefore $f(1) = k_{ji}^{\text{St}}$ and the function $f(x)$ searched for may have the form

$$f(x_i) = k_{ji}^{\text{St}} - F(1 - x_i). \quad (19)$$

The actual type of the dependence $F(1 - x_i)$ has, however, to be determined on the basis of the experimental data.

If the activity is defined using relation (18), then it holds

$$\lim_{x_i \rightarrow 1} \gamma_i = 1.$$

The value of γ_i can be determined by comparison of the theoretical and experimental liquidus course of the i -th component of the system.

D. Application of the universal relationship to the calculation of the liquidus course of NaCl in the system NaCl—M₃AlF₆

The advantage of using the universal relationship is evident especially in the change of the particle number, typical of systems containing cryolites. To prove this the theoretical liquidus course of NaCl in the system NaCl—M₃AlF₆ was calculated in two ways:

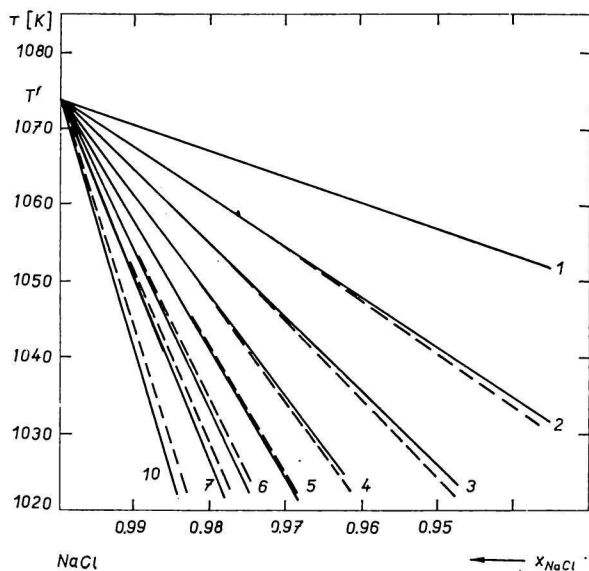


Fig. 1. Comparison of the theoretical course of the liquidus of NaCl in the systems NaCl—M₃AlF₆ calculated by means of the Temkin model (—), the universal relationship (---).

The numerals represent the exponent in eqn (2) and are equal to the number of ions arising in the dissociation of one molecule of M₃AlF₆ in the given system and being not present in pure molten NaCl.

by means of the Temkin model [2] and using the relationship (2) k_{ji} gaining the values of the integers 1, 2, 3, 4, 5, 6, 7, and 10. The graphical comparison of both results is in Fig. 1. It is clear that within the experimental inaccuracy both methods yield the same result, the calculation according to the universal relationship being essentially simpler.

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