

Cryometry on the basis of complex chemical compounds

II. The analysis of possible interactions in a binary system one component of which is a complex compound

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A binary system of ionic character composed of one simple and one complex compound is treated and the possible interactions in this system are analyzed. It is assumed that the simple compound brings into the melt of pure molten complex compound different number of cations and/or anions. It is proved that semiempirical relationships and rules which are used in cryometry of molten substances can be rationally derived.

Рассмотрена бинарная система ионного характера, состоящая из одного простого и одного сложного вещества; рассмотрены также возможные взаимодействия внутри этой системы. Полагается, что простое вещество вносит в расплав чистого комплексного соединения различное число катионов и/или анионов. Доказано, что возможно вывести рациональным путем полуэмпирические соотношения и правила, используемые в криометрии расплавленных веществ.

Application of the cryometric method in investigation of molten salts systems consists in determination of the value of the slope of tangent $k_0(i)$ to the liquidus curve of the substance i in the eutectic system $i-j$. No solid solutions must exist on the basis of the component i in the system. Then it holds

$$k_0(i) = \frac{R[T_f(i)]^2}{\Delta H_f(i)} \cdot k_{st}(j/i) \quad (1)$$

where $k_0(i)$ is the slope of tangent to the liquidus curve of the i -th component when the mole fraction of this component, $x(i)$, in solution tends to unit. $\Delta H_f(i)$ is the molar enthalpy of fusion of the component i . $k_{st}(j/i)$ is Stortenbeker's correction factor. It equals the number of species formed in the system of pure molten

substance *i* as the result of addition of one molecule of component *j*.

The semiempirical relationship (1) can be rationally derived from the LeChatelier—Shreder equation. From this equation it follows

$$k_0(i) = \lim_{x(i) \rightarrow 1} \frac{dT(i)}{dx(i)} = \frac{R[T_i(i)]^2}{\Delta H_f(i)} \lim_{x(i) \rightarrow 1} \frac{da(i)}{dx(i)} \quad (2)$$

$T(i)$ is the temperature of liquidus of component *i* in the system *i*—*j*. $x(i)$ is the mole fraction of component *i* in the liquid phase. $a(i)$ is the thermodynamic activity of component *i*. When $x(i) \rightarrow 1$, $a(i) \rightarrow x(i) \rightarrow 1$.

From comparison of eqns (1) and (2) we readily obtain the rational relationship for the semiempirical Stortenbeker's correction factor

$$k_{st}(j/i) = \lim_{x(i) \rightarrow 1} \frac{da(i)}{dx(i)} \quad (3)$$

Knowledge of the quantity $k_{st}(j/i)$ allows to judge on the character of dissociation of component *j* in the system *i*—*j* providing that the concentration of the substance *j* is sufficiently small.

As it has been shown in paper [1] when the component *i* corresponds to a complex compound *Z* with nonzero degree of thermal dissociation into simple compounds or elements then we can write for the slope of tangent $k_0(Z)$ to the liquidus curve of compound *Z* in the system *Z*—*R*

$$k_0(Z) = \lim_{x(Z) \rightarrow 1} \frac{dT(Z)}{dx(Z)} = \frac{R[T_i(Z)]^2}{\Delta H_f(Z)} \cdot \frac{1}{a_0(Z)} \cdot \lim_{x(Z) \rightarrow 1} \frac{da(Z)}{dx(Z)} \quad (4)$$

$T(Z)$ is the temperature of liquidus of compound *Z* in the system *Z*—*R*, $x(Z)$ is the mole fraction of "weight-in" compound *Z* in the solid mixture *Z* + *R*. $a_0(Z)$ is the activity of compound *Z* in the solution which is formed by melting of pure solid compound *Z*, i.e. when the mole fraction $x(Z)$ of the solid compound equals one. When the compound *Z* melts it thermally dissociates and the melt contains also products of this dissociation. Let us assume that in the melt of pure solid compound *Z* the mole fraction of nondissociated compound *Z* equals $x_0(Z)$. We choose $a_0(Z) = x_0(Z) < 1$.

Comparing eqns (1) and (4) we obtain in this case for Stortenbeker's factor the following rational relationship

$$k_{st}(R/Z) = \frac{1}{a_0(Z)} \lim_{x(Z) \rightarrow 1} \frac{da(Z)}{dx(Z)} \quad (5)$$

Now we shall consider interaction in the system *Z*—*R* where *Z* = *M_rCD* is the complex compound of the type (1 + 1) which partially undergoes the thermal dissociation into two completely stable anions denoted as *C⁻* and *D⁻*. Activities of substances in solution will be expressed on the basis of Temkin model [2]. In

writing the reaction schemes we will respect the fact that according to this model the magnitude of electrical charge of ions is not substantial. Together with thermal dissociation also the electrolytical dissociation takes place in the melt. We postulate that the melt formed after melting of pure compound Z consists of the mixture of ions M^+ , CD^- , C^- , and D^-

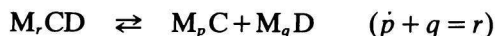
Further we assume that also the substance R which is added to the melt of substance Z has ionic character. We shall discuss four types of possible interactions of compounds Z and R:

1. Substance R brings no new (uncommon) species in the molten compound Z.
2. Substance R brings in the molten compound Z only anions as new species.
3. Substance R brings in the molten compound Z only cations as new species.
4. Substance R has no common species with the molten compound Z.

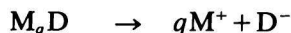
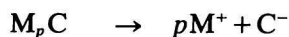
Our aim is to prove consistency in the theoretical approach to the topic of cryometry on the basis of complex compound. We will show that theoretical conclusions are in full agreement with the results which follow from experimental experience.

1. Substance R brings no new species into the melt resulting from melting of pure solid complex compound Z

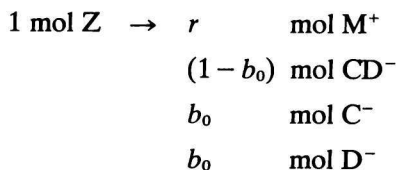
Let us consider complex compound $Z = M_rCD$ where M^+ is the cation and CD^- is the complex anion. The pure solid compound Z dissociates under melting both electrolytically and thermally. Formally we may write that compound Z after melting partially thermally dissociates according to the scheme



The thermally nondissociated complex compound $Z = M_rCD$ as well as the products of its thermal dissociation M_pC and M_qD dissociate completely electrolytically



When 1 mol of pure solid substance $Z = M_rCD$ melts, it forms



b_0 denotes the degree of thermal dissociation of pure complex compound Z at its melting temperature; $0 < b_0 < 1$.

For the sum of amount of substance of cations and anions it holds

$$\begin{aligned}n(\Sigma(\text{cation}))/\text{mol} &= r \\n(\Sigma(\text{anion}))/\text{mol} &= 1 + b_0\end{aligned}$$

For the activities of constituents in solution which is formed by melting of pure solid compound Z it holds

$$\begin{aligned}a_0(\text{Z}) &= x_0^r(\text{M}^+) \cdot x_0(\text{CD}^-) = x_0(\text{CD}^-) \\a_0(\text{M}_p\text{C}) &= x_0^p(\text{M}^+) \cdot x_0(\text{C}^-) = x_0(\text{C}^-) \\a_0(\text{M}_q\text{D}) &= x_0^q(\text{M}^+) \cdot x_0(\text{D}^-) = x_0(\text{D}^-)\end{aligned}$$

The quantities $a_0(\text{Z}) = a_0(\text{M}_r\text{CD})$, $a_0(\text{M}_p\text{C})$, and $a_0(\text{M}_q\text{D})$ denote the Temkin activities of corresponding substances in solution which results from melting of pure solid complex compound $\text{Z} = \text{M}_r\text{CD}$. It is seen that there is only one kind of cations in this system and thus $x_0(\text{M}^+) = 1$.

For the equilibrium constant of thermal dissociation, $K_0(\text{Z}, \text{dis})$ of pure compound Z it holds

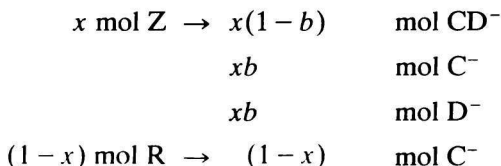
$$K_0(\text{Z}, \text{dis}) = \frac{a_0(\text{M}_p\text{C}) \cdot a_0(\text{M}_q\text{D})}{a_0(\text{M}_r\text{CD})} = \frac{x_0(\text{C}^-) \cdot x_0(\text{D}^-)}{x_0(\text{CD}^-)} \quad (6)$$

Since $x_0(\text{C}^-) = x_0(\text{D}^-) = b_0/(1 + b_0)$, $x_0(\text{CD}^-) = (1 - b_0)/(1 + b_0)$, it holds after rearrangement

$$K_0(\text{Z}, \text{dis}) = \frac{b_0^2}{1 - b_0^2} \quad (7)$$

Now we shall determine the equilibrium constant of thermal dissociation $K(\text{Z}, \text{dis})$ of compound Z in its mixture with substance R which brings no new species in the solution formed by melting of pure solid compound Z. With respect to the chosen scheme of dissociation of compound Z the substance R must be identical with substance M_pC or M_qD ($\text{R} = \text{M}_p\text{C}$ or $\text{R} = \text{M}_q\text{D}$).

Let us assume that $\text{R} = \text{M}_p\text{C}$. For melting process of the mixture consisting of x mol of pure solid compound Z and $(1 - x)$ mol of substance R it holds



The quantity b is the degree of thermal dissociation of complex compound Z in the molten mixture $\text{Z} + \text{R}$. From the physical point of view it must hold $0 < b < 1$. Generally also $b \neq b_0$.

With respect to the fact that in the system Z—R there is only one kind of cations, *i.e.* M^+ , it is sufficient in all dissociation schemes to consider only anions. For the sum of amount of substance of anions it holds

$$n(\Sigma(\text{anion}))/\text{mol} = x - xb + 2xb + 1 - x = 1 + xb$$

For the Temkin activities of constituents (substances) in the molten mixture Z + R it holds

$$a(Z) = a(M_rCD) = x(M_rCD) = x(CD^-) = \frac{x(1-b)}{1+xb} \quad (8)$$

$$a(M_pC) = x(M_pC) = x(C^-) = \frac{xb+1-x}{1+xb} \quad (9)$$

$$a(M_qD) = x(M_qD) = x(D^-) = \frac{xb}{1+xb} \quad (10)$$

For the equilibrium constant of thermal dissociation $K(Z, \text{dis})$ of complex compound Z in its mixture with substance R = M_pC it holds

$$K(Z, \text{dis}) = \frac{a(M_pC) a(M_qD)}{a(M_rCD)} = \frac{x(C^-) \cdot x(D^-)}{x(CD^-)} \quad (11)$$

The quantities $a(M_pC)$, *etc.* denote the Temkin activities of corresponding constituents in melt of the system Z + R. Introducing from eqns (8—10) into eqn (11) we obtain

$$K(Z, \text{dis}) = \frac{(xb+1-x)b}{(1-b)(1+xb)} \quad (12)$$

Let us assume that $K(Z, \text{dis}) = K_0(Z, \text{dis})$. This assumption is the more correctly fulfilled the more the mole fraction $x(Z)$ (related to solid mixture Z + R) tends to unit. In limit $x(Z) \rightarrow 1$ this equality holds precisely. Then we can write

$$\frac{(xb+1-x)b}{(1-b)(1+xb)} = \frac{b_0^2}{1-b_0^2} \quad (13)$$

or

$$b^2 + \frac{1-x}{x} b - \frac{b_0^2}{x} = 0 \quad (14)$$

It is seen that this is a quadratic equation with respect to b ; $b = f(x; b_0)$. It is apparent that only the solution which satisfies the condition $0 < b < 1$ has physical meaning. It readily follows

$$b = -\frac{1-x}{2x} + \left[\frac{(1-x)^2}{4x^2} + \frac{b_0^2}{x} \right]^{1/2} \quad (15)$$

When we introduce b as it follows from eqn (15) into eqn (8) we obtain

$$a(Z) = \frac{x + \frac{1-x}{2} - \left[\frac{(1-x)^2}{4} + xb_0^2 \right]^{1/2}}{1 - \frac{1-x}{2} + \left[\frac{(1-x)^2}{4} + xb_0^2 \right]^{1/2}}$$

This relationship can be simplified (we shall write a instead of $a(Z)$)

$$a = \frac{1+x - [(1-x)^2 + 4xb_0^2]^{1/2}}{1+x + [(1-x)^2 + 4xb_0^2]^{1/2}} \quad (16)$$

In the next we need to determine the expression da/dx (for simplicity we shall write dx instead of $dx(Z)$) and finally also $\lim(da/dx)$ for $x \rightarrow 1$ (we again write x instead of $x(Z)$).

At calculation of the expression da/dx we shall use the substitution $a = U/V$, where U denotes the numerator on the right-hand side of the fraction (16)

$$U = 1 + x - [(1-x)^2 + 4xb_0^2]^{1/2}$$

and V equals the denominator of the fraction (16)

$$V = 1 + x + [(1-x)^2 + 4xb_0^2]^{1/2}$$

It holds

$$\frac{da}{dx} = \frac{V \frac{dU}{dx} - U \frac{dV}{dx}}{V^2} \quad (17)$$

$$\frac{dU}{dx} = 1 - \frac{1}{2} [(1-x)^2 + 4xb_0^2]^{-1/2} \cdot [-2(1-x) + 4b_0^2] \quad (18)$$

$$\frac{dV}{dx} = 1 + \frac{1}{2} [(1-x)^2 + 4xb_0^2]^{-1/2} \cdot [-2(1-x) + 4b_0^2] \quad (19)$$

For the case $\lim x \rightarrow 1$ it holds

$$\lim \frac{da}{dx} = \frac{\lim V \cdot \lim \frac{dU}{dx} - \lim U \cdot \lim \frac{dV}{dx}}{(\lim V)^2} \quad (20)$$

Now we shall determine values of the corresponding limits

$$\lim U = 1 + 1 - 2b_0 = 2 - 2b_0 \quad (21)$$

$$\lim V = 1 + 1 + 2b_0 = 2 + 2b_0 \quad (22)$$

$$\lim \frac{dU}{dx} = 1 - \frac{1}{2} \cdot \frac{1}{2} b_0^{-1} \cdot 4b_0^2 = 1 - b_0 \quad (23)$$

$$\lim \frac{dV}{dx} = 1 + \frac{1}{2} \cdot \frac{1}{2} b_0^{-1} \cdot 4b_0^2 = 1 + b_0 \quad (24)$$

After introducing eqns (21–24) into eqn (20) we obtain

$$\lim \frac{da}{dx} = \frac{(2 + 2b_0)(1 - b_0) - (2 - 2b_0)(1 + b_0)}{(2 + 2b_0)^2}$$

or

$$\lim \frac{da}{dx} = \frac{(1 + b_0)(1 - b_0) - (1 - b_0)(1 + b_0)}{2(1 + b_0)^2} = 0 \quad (25)$$

After introducing eqn (25) into eqn (4) we find that

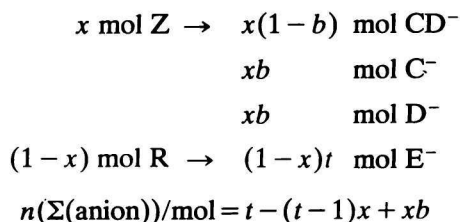
$$k_0 = \frac{R(T_t)^2}{\Delta H_t} \cdot \frac{1}{a_0} \lim \frac{da}{dx} = 0 \quad (26)$$

The relationship (26) holds regardless of the magnitude of a_0 , provided $a_0 \neq 0$, which is always fulfilled. Of course it must also hold $\Delta H_t \neq 0$. The latter condition is satisfied in the case of all phase transitions of the first order [3].

Validity of the relationship (26) means that the slope of the tangent to the liquidus curve of the complex compound $Z = M_rCD$ in its mixture with substance $R = M_pC$ equals zero. This is an exact proof of the semiempirical rule which states that the addition of substance R into molten substance Z causes in limit $x(Z) \rightarrow 1$ no decrease in the temperature of primary crystallization of the compound Z providing that the substance R does not bring in the melt of substance Z any new species. Simultaneously it means that in this case it is not possible to use the dependence of the temperature of liquidus of the compound Z on mole fraction $x(Z)$ for cryometric treatment.

2. Substance R having a common cation with the complex compound Z
brings in the system formed by melting of pure compound Z
totally t new particles (anions)

Let us consider the system Z—R, namely $M_rCD—ME_t$. For melting process of the mixture composed of x mol of pure solid substance Z and $(1-x)$ mol of substance R (the substances Z and R have a common cation) it holds



For the Temkin activities of species forming the molten mixture Z + R it holds

$$a(\text{Z}) = x(\text{CD}^-) = \frac{x(1-b)}{t - (t-1)x + xb} \quad (27)$$

$$a(\text{M}_p\text{C}) = a(\text{M}_q\text{D}) = x(\text{C}^-) = x(\text{D}^-) = \frac{xb}{t - (t-1)x + xb} \quad (28)$$

$$a(\text{ME}_t) = x'(\text{E}^-) = \left[\frac{(1-x)t}{t - (t-1)x + xb} \right]^t \quad (29)$$

After introducing from eqns (27) and (28) into eqn (11) we obtain for the equilibrium constant of thermal dissociation of the compound Z, $K(\text{Z}, \text{dis})$, in the melt with the substance $\text{R} = \text{ME}_t$, the relationship

$$K(\text{Z}, \text{dis}) = \frac{xb^2}{(1-b)[t - (t-1)x + xb]} \quad (30)$$

Let us assume again that $K(\text{Z}, \text{dis}) = K_0(\text{Z}, \text{dis})$. Then it holds

$$\frac{xb^2}{(1-b)[t - (t-1)x + xb]} = \frac{b_0^2}{1-b_0^2} \quad (31)$$

and it readily follows

$$b^2 + b \frac{1-x}{x} tb_0^2 + \frac{tx-x-t}{x} b_0^2 = 0$$

or

$$b = -\frac{1-x}{2x} tb_0^2 + \left[\frac{(1-x)^2}{4x^2} t^2 b_0^4 - \frac{tx-x-t}{x} b_0^2 \right]^{1/2} \quad (32)$$

We may insert b from eqn (32) into eqn (27). After rearrangement (we write a instead of $a(\text{Z})$) we get

$$a = \frac{2x + (1-x)tb_0^2 - [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{1/2}}{2t - 2(t-1)x - (1-x)tb_0^2 + [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{1/2}} \quad (33)$$

For calculation of the expression da/dx we shall use the substitution $a = U/V$, where U denotes the numerator and V the denominator, respectively, in the right-hand side of fraction (33).

It holds further

$$\begin{aligned} \frac{dU}{dx} &= 2 - tb_0^2 - \frac{1}{2} [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{-1/2} \cdot \\ &\quad \cdot [-2(1-x)t^2 b_0^4 - 4(2tx - 2x - t)b_0^2] \end{aligned} \quad (34)$$

$$\begin{aligned} \frac{dV}{dx} &= -2(t-1) + tb_0^2 + \frac{1}{2} [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{-1/2} \cdot \\ &\quad \cdot [-2(1-x)t^2 b_0^4 - 4(2tx - 2x - t)b_0^2] \end{aligned} \quad (35)$$

For the calculation of the expression $\lim da/dx$ when x tends to unit we shall use eqn (20). The values of the corresponding limits are following

$$\lim U = 2 - 2b_0$$

$$\lim V = 2 + 2b_0$$

$$\lim \frac{dU}{dx} = 2 - b_0(2 - t) - b_0^2 t$$

$$\lim \frac{dV}{dx} = -2(t - 1) + b_0(2 - t) + b_0^2 t$$

If we introduce these values into eqn (18) we get after rearrangement the relationship

$$\lim \frac{da}{dx} = \frac{1 - b_0}{1 + b_0} \cdot t \quad (36)$$

As we stated before (see eqn (27))

$$a = \frac{x(1 - b)}{t - (t - 1)x + xb}$$

If $x \rightarrow 1$, $a \rightarrow a_0$, $b \rightarrow b_0$

$$a_0 = \frac{1 - b_0}{1 + b_0} \quad (37)$$

In the way of introducing eqns (36) and (37) into eqn (4) we obtain after rearrangement

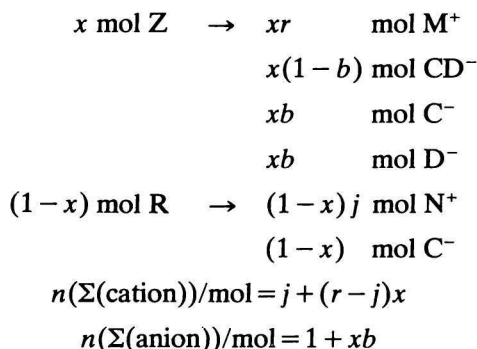
$$k_0 = \frac{RT_t^2}{\Delta H_t} \cdot t \quad (38)$$

The substance $R = ME_t$ brings in the system formed by molten pure complex compound $Z = M_rCD$ totally t new particles, viz. anions E^- . Therefore $k_{st}(R/Z) = t$. The same conclusion results when we insert eqns (36) and (37) in eqn (5). Therefore it can be stated that for the case of the system $M_rCD - ME_t$ the correctness of cryometry on the basis of complex compound $M_rCD = Z$ has been rationally proved.

3. Substance R having a common anion with the complex compound Z brings in the system formed by melting of pure compound Z totally j new particles (cations)

Let us consider the system $Z - R$, namely $M_rCD - N_jC$ or $M_rCD - N_jD$. We shall choose the first of these two equivalent possibilities. For melting process of the

mixture consisting of x mol of pure solid compound Z and $(1-x)$ mol of substance R it holds



For activities of corresponding constituents of the molten mixture Z + R it holds according to the Temkin model

$$a(\text{M}_r\text{CD}) = x^r(\text{M}^+) \cdot x(\text{CD}^-) = \left[\frac{xr}{j + (r-j)x} \right]^r \cdot \frac{x(1-b)}{1+xb} \quad (39)$$

$$a(\text{M}_p\text{C}) = x^p(\text{M}^+) \cdot x(\text{C}^-) = \left[\frac{xr}{j + (r-j)x} \right]^p \cdot \frac{xb + 1 - x}{1 + xb} \quad (40)$$

$$a(\text{M}_q\text{D}) = x^q(\text{M}^+) \cdot x(\text{D}^-) = \left[\frac{xr}{j + (r-j)x} \right]^q \cdot \frac{xb}{1 + xb} \quad (41)$$

$$a(\text{N}_j\text{C}) = x^j(\text{N}^+) \cdot x(\text{C}^-) = \left[\frac{(1-x)j}{j + (r-j)x} \right]^j \cdot \frac{xb + 1 - x}{1 + xb} \quad (42)$$

As $p + q = r$ it holds for $K(\text{Z, dis})$

$$K(\text{Z, dis}) = \frac{a(\text{M}_p\text{C}) \cdot a(\text{M}_q\text{D})}{a(\text{M}_r\text{CD})} = \frac{x(\text{C}^-) \cdot x(\text{D}^-)}{x(\text{CD}^-)}$$

After introducing we get

$$K(\text{Z, dis}) = \frac{(xb + 1 - x)b}{(1-b)(1+xb)} \quad (12)$$

which is the relationship identical with eqn (12). Further procedure is identical with the relationships (13–15). We can readily replace the expression $x(1-b)/(1+xb)$ in eqn (39) by the right-hand side of eqn (16). We get

$$a = \left[\frac{xr}{j + (r-j)x} \right]^r \cdot \frac{1+x - [(1-x)^2 + 4xb\delta]^1/2}{1+x + [(1-x)^2 + 4xb\delta]^1/2} \quad (43)$$

For the calculation of the expression da/dx we shall use the substitution

$$a = A \cdot \frac{U}{V}$$

$$A = \left[\frac{xr}{j + (r-j)x} \right]^r$$

$$U = 1 + x - [(1-x)^2 + 4xb_0^2]^{1/2}$$

$$V = 1 + x + [(1-x)^2 + 4xb_0^2]^{1/2} \quad (44)$$

It holds

$$\frac{da}{dx} = \frac{U}{V} \cdot \frac{dA}{dx} + A \frac{V \frac{dU}{dx} - U \frac{dV}{dx}}{V^2}$$

$$\frac{dA}{dx} = r \left[\frac{xr}{j + (r-j)x} \right]^{r-1} \cdot \frac{rj}{[j + (r-j)x]^2}$$

$$\frac{dU}{dx} = 1 - \frac{1}{2} [(1-x)^2 + 4xb_0^2]^{-1/2} \cdot [-2(1-x) + 4b_0^2]$$

$$\frac{dV}{dx} = 1 + \frac{1}{2} [(1-x)^2 + 4xb_0^2]^{-1/2} \cdot [-2(1-x) + 4b_0^2] \quad (45)$$

For the expression $\lim da/dx$ when $x \rightarrow 1$ it holds

$$\lim \frac{da}{dx} = \lim \frac{U}{V} \cdot \lim \frac{dA}{dx} +$$

$$+ \lim A \cdot \frac{\lim V \cdot \lim \frac{dU}{dx} - \lim U \cdot \lim \frac{dV}{dx}}{(\lim V)^2} \quad (46)$$

The corresponding limits are

$$\begin{array}{ll} \lim A = 1 & \lim dA/dx = j \\ \lim U = 2 - 2b_0 & \lim dU/dx = 1 - b_0 \\ \lim V = 2 + 2b_0 & \lim dV/dx = 1 + b_0 \end{array}$$

After introducing into eqn (46) we get after rearrangement

$$\lim \frac{da}{dx} = \frac{1 - b_0}{1 + b_0} \cdot j + \frac{(1 + b_0)(1 - b_0) - (1 - b_0)(1 + b_0)}{2(1 + b_0)^2} \quad (47)$$

Value of the expression $\lim da/dx$ (and in accordance with eqn (4) also of the expression $\lim dT/dx$) is given by the sum of two terms. The first term corresponds to the contribution of noncommon cations which are introduced in the melt of pure

compound Z by the substance R, while the second term depends on the contribution of noncommon anions of substance R. In this case we postulated that substance R and substance Z have only noncommon cations. Thus the second term must be zero from physical principle, which is in full agreement with eqn (47).

Definitively it holds

$$\lim \frac{da}{dx} = \frac{1 - b_0}{1 + b_0} j = a_0 \cdot j \quad (48)$$

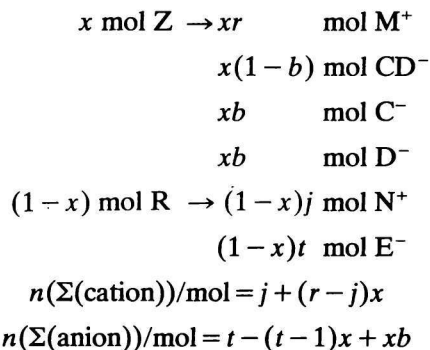
After introducing eqn (48) into eqn (4) we get

$$k_0 = \frac{RT_f^2}{\Delta H_f} \cdot j \quad (49)$$

Substance R = N_jC brings in the system formed by pure compound Z = M_rCD totally *j* new particles, viz. cations N⁺. Therefore *k_{st}*(R/Z) = *j*. The same result will be obtained when we insert eqns (37) and (48) in eqn (5). Thus in the case of the system M_rCD—N_jC the correctness of cryometry on the basis of complex compound M_rCD = Z has been proved.

4. Substance R which has no common ion with the complex compound Z brings in the solution formed by melting of pure solid compound Z totally *q* new particles, viz. *j* cations and *t* anions

Let us consider the system Z—R, namely M_rCD—N_jE_t. For melting process of the mixture composed of *x* mol of pure solid compound Z and (1 - *x*) mol of substance R it holds



For the Temkin activities of corresponding species in the molten mixture Z + R it holds

$$a_{\text{M}_r\text{CD}} = x^r (\text{M}^+) \cdot x (\text{CD}^-) = \left[\frac{xr}{j + (r - j)x} \right]^r \cdot \frac{x(1 - b)}{t - (t - 1)x + xb} \quad (50)$$

$$a(M_p C) = x^p(M^+) \cdot x(C^-) = \left[\frac{xr}{j + (r-j)x} \right]^p \cdot \frac{xb}{t - (t-1)x + xb} \quad (51)$$

$$a(M_q D) = x^q(M^+) \cdot x(D^-) = \left[\frac{xr}{j + (r-j)x} \right]^q \cdot \frac{xb}{t - (t-1)x + xb} \quad (52)$$

$$a(N_j E_r) = x^j(N^+) \cdot x^r(E^-) = \left[\frac{(1-x)j}{j + (r-j)x} \right]^j \cdot \left[\frac{(1-x)t}{t - (t-1)x + xb} \right]^r \quad (53)$$

After introducing eqns (50—52) into eqn (11) we find out that

$$K(Z, \text{dis}) = \frac{xb^2}{(1-b)[t - (t-1)x + xb]} \quad (30)$$

which is identical with eqn (30). Further procedure can be represented by the equations which are identical with the relationships (31) and (32). Thus we can replace in eqn (50) the expression $xb/[t - (t-1)x + xb]$ with the right-hand side of eqn (33) and we get

$$a = \left[\frac{xr}{j + (r-j)x} \right]^r \cdot \frac{2x + (1-x)tb_0^2 - [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{1/2}}{2t - 2(t-1)x - (1-x)tb_0^2 + [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{1/2}} \quad (54)$$

For the next calculation we shall use the substitution which is defined by eqn (44)

$$A = \left[\frac{xr}{j + (r-j)x} \right]^r$$

$$U = 2x + (1-x)tb_0^2 - [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{1/2}$$

$$V = 2t - 2(t-1)x - (1-x)tb_0^2 + [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{1/2}$$

Further it holds

$$\frac{dA}{dx} = r \left[\frac{xr}{j + (r-j)x} \right]^{r-1} \cdot \frac{rj}{[j + (r-j)x]^2}$$

$$\frac{dU}{dx} = 2 - tb_0^2 - \frac{1}{2} [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{-1/2} \cdot [-2(1-x)t^2 b_0^4 - 4(2tx - 2x - t)b_0^2]$$

$$\frac{dV}{dx} = -2(t-1) + tb_0^2 + \frac{1}{2} [(1-x)^2 t^2 b_0^4 - 4(tx^2 - x^2 - tx)b_0^2]^{-1/2} \cdot [-2(1-x)t^2 b_0^4 - 4(2tx - 2x - t)b_0^2]$$

For calculation of the expression $\lim da/dx$ for $x \rightarrow 1$ we shall use the relationship (46). The corresponding limits are as follows

$$\begin{aligned}\lim A &= 1 \\ \lim U &= 2 - 2b_0 \\ \lim V &= 2 + 2b_0 \\ \lim dA/dx &= j \\ \lim dU/dx &= 2 - (2-t)b_0 - b_0^2t \\ \lim dV/dx &= -2(t-1) + (2-t)b_0 - b_0^2t\end{aligned}$$

After introducing into eqn (46) and rearrangement we get

$$\lim \frac{da}{dx} = \frac{1-b_0}{1+b_0} \cdot j + \frac{1-b_0}{1+b_0} \cdot t \quad (55)$$

or

$$\lim \frac{da}{dx} = \frac{1-b_0}{1+b_0} \cdot (j+t) = a_0(j+t) \quad (56)$$

Introducing this result into eqn (4) we obtain the expression

$$K_0(Z) = \frac{R[T_f(Z)]^2}{\Delta H_f(Z)} \cdot (j+t) \quad (57)$$

Substance $R = N_jE_t$, when it totally electrolytically dissociates, brings in the system formed by molten pure complex compound $Z = M_rCD$ totally q new particles, viz. j cations N^+ and t anions E^- ; $j+t=q$. Therefore $k_{st}(R/Z) = q$. It is the same expression which we obtain by replacing a_0 and $\lim da/dx$ (for $x \rightarrow 1$) in eqn (5).

As we have already pointed out application of the Temkin model for calculation of activities of corresponding constituents in the derivation of the cryometric relationships reflects very remarkably the influence of the noncommon ions in substance R on the value of the expression $\lim da/dx$ on the side of compound Z . The method of calculation of $\lim da/dx$ as the limit of the expression AU/V has not only the character of a mathematical rearrangement but it has also physical background. The term A is related to the noncommon cations of substance R while the term U/V to the noncommon anions.

In this paper it has been assumed that in the system $Z-R$ the complex compound $Z = M_r(CD)$ exists. The phenomenon of the partial thermal dissociation, which is characterized by the degree of dissociation, viz. b_0 , relates to the complex anion $(CD)^-$. The result of this assumption is the nonsymmetrical form of the right-hand side of eqns (45) and (46). The term which reflects the effect of the noncommon cations is substantially more simple than that corresponding to the effect of noncommon anions.

If assuming the existence of a complex cation, which undergoes a partial thermal dissociation at melting, the corresponding expression would obtain an "inverse" form.

Regardless of the asymmetry of the right-hand side of eqns (45) and (46), after introducing the corresponding terms the symmetrical eqn (55) results. It means that the effective contribution to the depression of the liquidus temperature of complex compound at $x \rightarrow 1$ caused by noncommon cations is quite equivalent to that caused by noncommon anions.

Similar result can be obtained by the direct application of the Temkin model for derivation of activities of the complex compound Z in the given system. It holds

$$a(\text{M}, \text{CD}) = x^r(\text{M}^+) \cdot x(\text{CD}^-)$$

and hence

$$\frac{da(\text{M}, \text{CD})}{dx(\text{M}, \text{CD})} = x(\text{CD}^-) \cdot \frac{d[x^r(\text{M}^+)]}{dx(\text{M}, \text{CD})} + x^r(\text{M}^+) \cdot \frac{dx(\text{CD}^-)}{dx(\text{M}, \text{CD})}$$

For the expression $\lim da(\text{M}, \text{CD})/dx(\text{M}, \text{CD})$ when $x(\text{M}, \text{CD}) \rightarrow 1$ it holds

$$\begin{aligned} \lim \frac{da(\text{M}, \text{CD})}{dx(\text{M}, \text{CD})} &= \lim x(\text{CD}^-) \cdot \lim \frac{d[x^r(\text{M}^+)]}{dx(\text{M}, \text{CD})} + \\ &+ \lim x^r(\text{M}^+) \cdot \lim \frac{dx(\text{CD}^-)}{dx(\text{M}, \text{CD})} \end{aligned} \quad (58)$$

The first term on the right-hand side of eqn (58) corresponds to the contribution of noncommon cations of substance R, while the second term reflects the contribution of the noncommon anions to the value of the expression $da(\text{Z})/dx(\text{Z})$ and, therefore, also to the expression $\lim da(\text{Z})/dx(\text{Z})$ for $x(\text{Z}) \rightarrow 1$.

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