

Cryometry on the basis of complex chemical compounds

I. Derivation of the basic cryometric relationship

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The "classical" relationship for cryometry on the basis of substance i in the system $i-j$ is discussed. It is shown that if the substance i dissociates, the "classical" cryometric relationship loses its validity and it is necessary to apply a new relationship which is more general.

Обсуждается «классическое» соотношение для криометрии на основе вещества i в системе $i-j$. Показано, что если вещество i диссоциирует, «классическое» криометрическое соотношение становится неприменимым и становится необходимым применить новое более общее соотношение.

The principle of cryometric method carried out on the basis of substance i in the eutectic system $i-j$ follows from the classical (semiempirical) cryometric relationship [1]

$$k^0(i) = \frac{R[T^f(i)]^2}{\Delta h^f(i)} k^{St}(j/i) \quad (1)$$

$k^0(i)$ is the slope of tangent to the liquidus curve of substance i in its melting point $T^f(i)$, $\Delta h^f(i)$ is the molar enthalpy of fusion of substance i , $k^{St}(j/i)$ is the Stortenbeker's correction factor which is numerically equal to the number of new (foreign) species which are formed in pure liquid of substance i by introducing one molecule of substance j . Limiting solid solutions formed on the basis of substance i must not be present. Further it is assumed that the substance i is thermally stable.

If, e.g. $i \equiv MA$, $j \equiv N_rB_t$ (M , N are the cations and A , B the anions) and these substances electrolytically dissociate according to the schemes $MA \rightarrow M^+ + A^-$, $N_rB_t \rightarrow r N^{u+} + t B^{w-}$, then one molecule of the substance j introduces into the pure liquid i $(r+t)$ new particles; $k^{St}(j/i) = r+t$. We need to know two from the quantities $k^0(i)$, $\Delta h^f(i)$, $k^{St}(j/i)$ in order to be able to calculate from eqn (3) the missing third quantity.

The empirical relation (1) can be readily derived from the simplified LeChatelier—Shreder equation

$$T = \frac{\Delta h^f(i)}{\frac{\Delta h^f(i)}{T^f(i)} - R \ln a(i)} \quad (2)$$

From this equation it follows that

$$k^0(i) = \lim_{x(i) \rightarrow 1} \frac{dT}{dx(i)} = \frac{R[T^f(i)]^2}{\Delta h^f(i)} \lim_{x(i) \rightarrow 1} \frac{da(i)}{dx(i)} \quad (3)$$

The symbol $a(i)$ in eqns (2) and (3) designates thermodynamic activity of substance i along its liquidus curve (the solution is in equilibrium with pure solid substance i). As standard state we chose the pure liquid substance i at temperature (and pressure) of the system. If the mole fraction $x(i)$ of substance i tends to one, $a(i) \rightarrow x(i) \rightarrow 1$. Let $i \equiv \text{MA}$, $j \equiv \text{N}_i\text{B}_i$, and let us assume a solution composed from x_1 moles of substance MA and x_2 moles of substance N_iB_i ($x_1 + x_2 = 1$). According to Temkin's model [2, 3] it holds for the activity of substance MA in solution

$$a(\text{MA}) = x(\text{M}^+) \cdot x(\text{A}^-) = \frac{x_1^2}{[r - x_1(r - 1)] \cdot [t - x_1(t - 1)]} \quad (4)$$

The symbols $x(\text{M}^+)$, $x(\text{A}^-)$ in eqn (4) denote the ionic fractions of cations M^+ and anions A^- .

It holds that

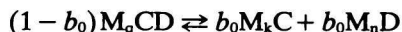
$$\lim_{x_1 \rightarrow 1} \frac{da(\text{MA})}{dx_1} = k^{\text{St}}(j/i) = r + t \quad (5)$$

After introducing this result in eqn (3) we derived rationally the relationship (1). Comparison of eqns (1) and (3) leads to the identity

$$k^{\text{St}}(j/i) = \lim_{x(i) \rightarrow 1} \frac{da(i)}{dx(i)} \quad (6)$$

More complicated situation arises when we have to theoretically prove the correctness of cryometry carried out on the basis of substance i in the system i — j when i is a complex substance Z which partially dissociates at melting to its original components.

Let $Z = \text{M}_q\text{CD}$ (C , D are the anions) and let the thermal dissociation proceed according to the scheme



where b_0 is the degree of thermal dissociation of pure substance Z ; $0 < b_0 < 1$. It

further holds that $q = k + n$. Therefore if we have pure solid substance Z at the beginning we obtain after its melting a solution containing three substances, viz. undissociated compound $Z = M_qCD$ and the products of its thermal dissociation M_kC and M_nD . Mole fraction of the liquid undissociated compound Z (it is denoted $y^0(Z)$) equals obviously $(1 - b_0)/(1 + b_0) < 1$. If we choose the state of this liquid undissociated compound Z as the standard, then $a^0(Z) = y^0(Z) = (1 - b_0)/(1 + b_0)$.

Generally it holds that the activity $a(Z)$ of compound Z along its liquidus curve is a function of degree of thermal dissociation b of the substance Z in solution with substance j . If it holds that $a(Z) = f(b)$ then also $da(Z)/dx(Z) = F(b)$; $x(Z)$ is the weighed-in mole fraction of the substance Z in the system $i-j$. If the identity (6) were still valid then also the factor $k^{st}(j/i)$ would have to be a function of the quantity b , which is not true. In our case $i = M_qCD$, $j = N_rB_t$ and therefore $k^{st}(j/i) = r + t \neq \varphi(b)$. It means that if the substance i is a complex compound Z with the above-mentioned properties, the identity (6) loses its validity.

Derivation of a general relationship for cryometry

According to *Glasstone* [4] the activity $a(Z)$ of compound Z along its liquidus curve obeys the relationship

$$\ln a(Z) = \frac{\Delta h^f(Z)}{R} \left[\frac{1}{T^f(Z, \text{hyp})} - \frac{1}{T} \right] \quad (7)$$

where $T^f(Z, \text{hyp})$ is the hypothetical temperature of fusion of thermally absolutely undissociated complex compound Z . In the relationship (7) we neglect the temperature dependence of the quantity $\Delta h^f(Z)$. This simplification, however, has no influence on the correctness of final result.

We may apply eqn (7) to the melting point of pure solid compound Z . Then

$$\ln a^0(Z) = \frac{\Delta h^f(Z)}{R} \left[\frac{1}{T^f(Z, \text{hyp})} - \frac{1}{T^f(Z, \text{exp})} \right] \quad (8)$$

where $T^f(Z, \text{exp})$ is the experimentally obtained temperature of fusion of pure solid compound Z . Combining eqns (7) and (8) we obtain

$$T^f(Z, \text{hyp}) = \frac{\Delta h^f(Z)}{\frac{\Delta h^f(Z)}{T^f(Z, \text{exp})} + R \ln a^0(Z)} \quad (9)$$

From eqn (7) we can explicitly express $T = f[\Delta h^f(Z), T^f(Z, \text{hyp}), \ln a(Z)]$, where $a(Z)$ is a function of mole fraction $x(Z)$ of pure compound Z weighed in the binary

mixture $Z-j$. Then it holds

$$k^0(Z) = \lim_{x(Z) \rightarrow 1} \frac{dT}{dx(Z)} = \frac{R \Delta h^f(Z)}{\left[\frac{\Delta h^f(Z)}{T^f(Z, \text{hyp})} - R \ln a^0(Z) \right]^2} \cdot \frac{1}{a^0(Z)} \cdot \lim_{x(Z) \rightarrow 1} \frac{da(Z)}{dx(Z)} \quad (10)$$

If $x(Z) \rightarrow 1$, then $T \rightarrow T^f(Z, \text{exp})$ and $a(Z) \rightarrow a^0(Z)$.

When we introduce $T^f(Z, \text{hyp})$ from eqn (9) we obtain after rearrangement

$$k^0(Z) = \lim_{x(Z) \rightarrow 1} \frac{dT}{dx(Z)} = \frac{R[T^f(Z, \text{exp})]^2}{\Delta h^f(Z)} \cdot \frac{1}{a^0(Z)} \cdot \lim_{x(Z) \rightarrow 1} \frac{da(Z)}{dx(Z)} \quad (11)$$

Eqn (11) is the general relationship for determination of the tangent of slope to the liquidus curve of complex compound Z in the system $Z-j$ in the limit $T \rightarrow T^f(Z, \text{exp})$. It differs from the classical relationship (3) by the term $a^0(Z)$. By comparison of eqns (1) and (11) we obtain for the Stortenbeker's correction factor $k^{\text{St}}(j/i)$ (we consider the case when i is a complex compound with nonzero degree of thermal dissociation)

$$k^{\text{St}}(j/i) = \frac{1}{a^0(i)} \cdot \lim_{x(i) \rightarrow 1} \frac{da(i)}{dx(i)} \quad (12)$$

Eqns (1) and (3) are therefore only special cases of the more general relationships (11) and (12).

References

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