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THE CLASSICAL CRYOMETRY IN TERNARY SYSTEMS

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The cryometry is one of significant theoretical and experimental methods of equilibrium investigation in the condensed systems. This method enables to obtain prevailably the value of melting enthalpy of the component A in a system A - B, if this system fulfills certain conditions. One of recently formed branches of cryometry is its extension to the ternary systems. It is based on the cryometry of binary eutectic mixture A + B, to which the third component C is added. From the analogy with classical cryometry it follows that the value of molar melting enthalpy of a eutectic mixture of substances A + B can be obtained by this method. For this value, which can be denoted as $\Delta H^{f,e}(A+B)$, it is valid

$$\Delta H^{f,e}(A+B) = x^{e}(A).\Delta H^{l,e/o,s}(A) + x^{e}(B).\Delta H^{l,e/o,s}(B) \qquad /1/$$

where $x^{e}(A)$, $x^{e}(B)$ are the concentration coordinates of a eutectic point $\underline{e}$ in a system A - B; $x^{e}(A) + x^{e}(B) = 1$.

$\Delta H^{l,e/o,s}(A)$, $\Delta H^{l,e/o,s}(B)$ are partial molar enthalpies of melting of components A and B in the eutectic point $\underline{e}$. These partial molar melting enthalpies are included in the relationship derived by Dodé and Hagège[1]

$$x^{e}(A).\Delta H^{l,e/o,s}(A).k^{e}(A) = x^{e}(B).\Delta H^{l,e/o,s}.k^{e}(B) \qquad /2/$$

$k^{e}(A)$, $k^{e}(B)$ are the slopes of tangents to the liquidus curves of the components A and B in the eutectic point $\underline{e}$ of the simple eutectic system A - B.

If we know the quantity $\Delta H^{f,e}(A+B)$ and the line slopes $k^{e}(A)$ and $k^{e}(B)$, we can calculate so the partial molar melting enthalpies $\Delta H^{l,e/o,s}(A)$, $\Delta H^{l,e/o,s}(B)$, as the partial molar mixing enthalpies $\Delta H^{l,e/o,l}/A,mix)$, resp.$\Delta H^{l,e/o,l}(B,mix)$ in the point $\underline{e}$.

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The relationship /2/ has been used in the simplified form by the proof of experimentally obtained phase diagrams for their principle correctness.

While the theoretical part of cryometry in binary systems has been postulated round in 1900, theory of cryometry in ternary systems has been given by Förland [2] at 1964. He supposed, that one molecule of the third component brings into the eutectic mixture, which is the basis where in the cryometry is realized, only one new particle. The result of his analysis shows that for the temperature decrease of the liquidus of binary eutectic mixture AC + BC under the influence of addition of the third substance MC , when the values of x(MC) are small, the relationship /3/ is valid; in the limiting state, for x(MC)⟶0, the relation /4/ is valid.

$$\frac{dT(AC+BC)}{dx(MC)} = - \frac{R.T.T^{e}}{\Delta H^{f,e}(AC+BC)} \qquad /3/$$

$$\lim_{x(MC)\to 0} \frac{dT}{dx(MC)} = - \frac{R.(T^{e})^{2}}{\Delta H^{f,e}(AC+BC)} \qquad /4/$$

When we consider a system A - B, where the molecule B brings into the pure substance A only one new particle and where on the basis of the substance A no solid solutions are formed, then for the limiting temperature gradient of liquidus of component A the relation /5/ takes place.

$$\lim_{x(A)\to 1} \frac{dT(A)}{dx(A)} = \frac{R/T^{f}(A)/^{2}}{\Delta H^{f}(A)} \qquad /5/$$

Because x(A) + x(B) = 1, dx(A) = - dx(B) and we obtain

$$\lim_{x(B)\to 0} \frac{dT(A)}{dx(A)} = \frac{R/T^{f}(A)/^{2}}{\Delta H^{f,e}(A)} \qquad /6/$$

Between the relations /4/ and /6/ is formally the total agreement.

Haase and Schönert in 1969 have very precisely derived the fundamental relationship for the cryometry in ternary systems [3]. Their derivation is general i.e. it is valid also for the case when the molecule of the third component C brings into the eutectics A + B together "k" new particles:

$$\lim_{x(C)\to 0} \frac{dT}{dx(C)} = - \frac{R(T^{e})^{2}}{\Delta H^{f,e}(A+B)} \cdot k \qquad /7/$$

It is evident, that the Förland's relationship is the extraordinary case of the relationship /7/.

Fellner and Matiašovský [4] in 1974 have applied quite different derivation of the fundamental relation for cryometry in three-component systems, supposing these two simplifications:

1. the system is ideal, $a(i) = x(i)$;
2. $\triangle H^f(A,B) \neq f(T)$

They advise upon the condition of correctness of cryometry that it is fulfilled for the ideal systems only when $\triangle H^f(A) = \triangle H^f(B)$.

For the derivation of the fundamental cryometric relation Malinovský [5] has taken the Gibbs-Duhem's and Le Chatelier-Shreder equations as the basis of considerations. In the latter case the derivation is done by exertion of isothermic-isobaric $\triangle G(T,P)$ cycle. In both cases the derivation leads to relations which are identical with /7/.

The successful realization of cryometric method in three-component systems is not limited for systems with a simple eutectics. The conditions are fulfilled also in such case when only binary system A - B has the simple eutectic character and when ternary system A - B - C only small surrounding of the liquidus of monovariant equilibrium shows no solid solutions.

Fellner and Matiašovský have found, as it has been before mentioned, that the condition of correct cryometry in ideal systems is $\triangle H^f(A) = \triangle H^f(B)$. This condition is but very strict. If it would be valid rigorously in that sense, that also relatively small difference between $\triangle H^f(A)$ and $\triangle H^f(B)$ would be lead to obtain incorrect values for the quantity $\triangle H^{f,e}(A+B)$, it would ment that the applicability of cryometric method would be substantially reduced in the case of three-component systems.

We have investigated the case, when the condition of correctness of cryometry in three-component system is not fulfilled and what influence it occurs to the quantity $\triangle H^{f,e}(A+B)$. As the method of this analysis we have used the method of theoretical experiment. We have taken these steps:

1. For the components A nad B the values of $T^f(i)$ and $\triangle H^f(i)$ were chosen
2. Applying Le Chatelier-Shreder equation we have calculated the course of liquidus curves of components A and B in binary system A - B also for $T(i) < T^e(A+B)$ and we have determined the coordi-

nates of the eutectic point of system A - B. The course of liquidus lines was calculated under the assumption that $x(i) = a(i)$; $\Delta H^{f}(i) = \Delta H^{o,l/o,s}(i)$.

3.From the calculated values $x(A)$ and $x(B)$ for $T(i) < T^{e}(A+B)$ we have found the value $x(C)$; $x(A) + x(B) + x(C) = 1$.

4. Taking these three known values $x(A)$, $x(B)$, $x(C)$ we have constructed the curves of monovariant equilibrium.

For the found $x(C)$ we have determined ΔT and calculated cryometrically $\Delta H^{f,e}(A+B)$.

5.The values $\Delta H^{f,e}(A+B)$ calculated in such way were compared with the ideal melting enthalpy of the system A - B in the eutectic point.

Applying the methods of theoretical experiment we have confirmed that if the condition of equality of melting enthalpies of the substances A and B is not fulfilled, it has not substantial influence on the accuracy of determination of the quantity $\Delta H^{f,e}(A+B)$, which is the basis for realization of cryometry.

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