Cryometry in ternary systems

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Cryometry on the basis of binary eutectic mixture as a method for determination of partial molar enthalpies of fusion and partial molar enthalpies of mixing of components of the binary mixture is discussed. The relationships for cryometry on the basis of binary eutectic mixture are derived and it is pointed out that cryometry can be carried out also in the systems forming solid solutions. Conditions for correctness of cryometry in ternary systems are analyzed. From this thermodynamic analysis it follows that in ideal systems cryometry on the basis of binary eutectic mixture can be carried out successfully providing the molar enthalpies of fusion of the components of the binary mixture equal. However, from numerical examples it follows that even if the conditions for correctness of the cryometric method are not strictly fulfilled accuracy of the determination of the enthalpy of fusion of eutectic mixture from cryometric data may be influenced only negligibly.

Обсуждается возможность использования криометрии на основе бинарной эвтектической смеси в качестве метода для определения парциальных мольных энтальпий плавления и парциальных мольных энтальпий смешения компонентов бинарной смеси. Выведены соотношения для криометрии на основе бинарной эвтектической смеси и отмечено, что криометрия может быть проведена также в системах, образующих твердые растворы. Анализируются условия применимости криометрии в тройных системах. Из проведенного термодинамического анализа следует, что в идеальных системах может быть успешно проведена криометрия на основе бинарной эвтектической смеси, в случае если величины мольных энтальпий плавления компонентов бинарной смеси одинаковы. Однако, исходя из численных примеров следует, что даже в случае не абсолютно строгого выполнения условий применимости криометрического метода, точность определения энтальпий плавления эвтектической смеси на основе криометрических данных подвержена лишь пренебрежительно малому влиянию.

As it follows from a number of publications and monographs [1, 2] cryometry is one of the very important theoretical-experimental methods for investigation of

equilibria in condensed systems. The monograph by *Petit* [2] is devoted specially to molten systems. If the investigated system fulfils certain conditions cryometric method allows to obtain the value of the enthalpy of fusion of the component A in the system A—B and it provides us with important information on the mechanism of thermal dissociation of complex anions [3]. It has been proved that cryometry can be carried out also on the basis of a complex compound with nonzero degree of thermal dissociation [4].

Recently the cryometric method has been applied also to the ternary systems. In this case the third component C is added to the binary eutectic mixture A + B. From the analogy with classical cryometric method it follows that we can obtain in this way the value of the molar enthalpy of fusion of the eutectic mixture of the substances A + B. If we denote this quantity as $\Delta H(\text{fus}, A + B, E)$ it holds

$$\Delta H(\text{fus}, A + B, E) = x(A, E) \cdot \Delta \bar{H}(A, (l, E/s^o)) +$$
$$+ x(B, E) \cdot \Delta \bar{H}(B, (l, E/s^o)) \tag{1}$$

where $x(A, E)$, $x(B, E)$ are the concentration coordinates of the eutectic point E in the system A—B; $x(A, E) + x(B, E) = 1$. $\Delta \bar{H}(i, (l, E/s^o))$ are the partial molar enthalpies of fusion of the components A and B at the eutectic point E. These partial molar enthalpies of fusion occur also in the relationship which has been derived by *Dodé* and *Hagège* [5]

$$x(A, E) \cdot \Delta \bar{H}(l, E/s^o) \cdot k(A, E) = x(B, E) \cdot \Delta \bar{H}(l, E/s^o) \cdot k(B, E) \tag{2}$$

where $k(A, E)$, $k(B, E)$ are the slopes of tangents to the liquidus curves of the components A and B at the eutectic point E. (A simple eutectic system A—B is assumed.)

If we know the quantity $\Delta H(\text{fus}, A + B, E)$ and the slopes $k(A, E)$, $k(B, E)$ we can calculate the partial molar enthalpies of fusion $\Delta \bar{H}(i, (l, E/s^o))$ as well as the partial molar enthalpies of mixing $\Delta \bar{H}(i, (l, E/l^o), \text{mix})$ at the point E [6]. The relationship (2) has been used in a simplified form for the verifying principal correctness of the experimental phase diagrams [7, 8].

While the theoretical background of cryometry in binary systems has been derived in about 1900 the theory of cryometry in ternary systems has been published by *Førland* only in 1964 [9]. Førland discussed the case when one molecule of the third component brings only one new species in the eutectic mixture. In this case the addition of the third substance MC (its mole fraction is denoted $x(\text{MC})$) decreases the temperature of liquidus of the eutectic mixture AC + BC according to the relationship

$$\frac{dT(AC + BC)}{dx(\text{MC})} = -\frac{RT\,T(E)}{\Delta H(\text{fus}, AC + BC, E)} \tag{3}$$

In the limit for $x(\text{MC}) \to 0$ it holds

$$\lim_{x(MC)\to 0} \frac{dT}{dx(MC)} = -\frac{R(T(E))^2}{\Delta H(fus, AC+BC, E)} \tag{4}$$

Let us consider the binary system A—B in which each molecule of the substance B brings in the pure substance A just one new species. We assume that the substance B does not form solid solution in A. Then for the limit temperature gradient of the liquidus of component A it holds

$$\lim_{x(A)\to 1} \frac{dT(A)}{dx(A)} = \frac{R(T(fus, A))^2}{\Delta H(fus, A)} \tag{5}$$

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

$$\lim_{x(B)\to 0} \frac{dT(A)}{dx(A)} = -\frac{R(T(fus, A))^2}{\Delta H(fus, A)} \tag{6}$$

It follows that there is a formal identity between the relationships (4) and (6).

In 1969 *Haase* and *Schönert* [10] derived in a very precise way the basic relationship for cryometry in ternary systems. Their relationship holds generally, *i.e.* also in the case when molecule of the third component C brings in the eutectic mixture A + B "*k*" new (foreign) species. It holds

$$\lim_{x(C)\to 0} \frac{\Delta T}{x(C)} = \frac{R(T(E))^2}{\Delta H(fus, A+B, E)} \cdot k \tag{7}$$

Because $\Delta T = T(E) - T$, $d\Delta T = -dT$ and by differentiation of the left-hand side of eqn (7) we obtain

$$\lim_{x(C)\to 0} \frac{dT}{dx(C)} = -\frac{R(T(E))^2}{\Delta H(fus, A+B, E)} \cdot k \tag{8}$$

Thus the relationship derived by Førland (4) is a special case of the relationship (8) for $k = 1$.

In 1974 *Fellner* and *Matiašovský* [11] derived the basic relationship for cryometry in ternary systems in different way. They made two simplifying assumptions:

i) the system is ideal (*i.e.* $a(i) = x(i)$),
ii) $\Delta H(fus, A, B) \neq f(T)$.

Authors of the cited paper [11] point out that the condition for correctness of cryometry given by Førland, *viz.* that the curve of monovariant equilibrium starting at the point E must, at least in the vicinity of point E, go towards the vertex C (Fig. 1) is fulfilled for ideal systems only when $\Delta H(fus, A) = \Delta H(fus, B)$.
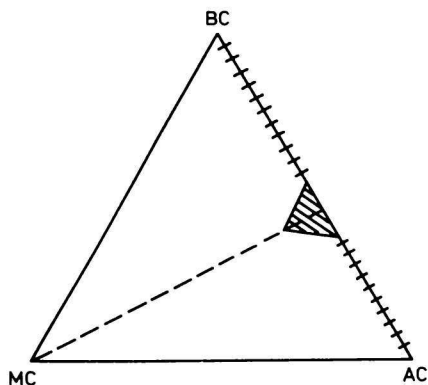
Fig. 1. Cryometry in a ternary system on the
basis of the binary system AC—BC.
Cross-hatched area contains no solid solutions.

A new method of derivation of the basic cryometric relationship

Gibbs—Duhem equation for the ternary system at constant T, p reads

$$x(A) \cdot d\bar{G}(A) + x(B) \cdot d\bar{G}(B) + x(C) \cdot d\bar{G}(C) = 0 \qquad (9)$$

It holds

$$x(A) + x(B) + x(C) = 1$$

Because $G(i) = G^0(i) + RT \ln a(i)$ we get after rearrangement

$$x(A) \cdot d \ln a(A) + x(B) \cdot d \ln a(B) = -x(C) \cdot d \ln a(C) \qquad (10)$$

Differential form of the Le Chatelier—Shreder equation is

$$d \ln a(i) = \frac{\Delta H(i, l^0/s^0)}{RT^2} dT \qquad (11)$$

We can insert the right-hand side of this equation for $i = A, B$ into eqn (10)

$$x(A) \frac{\Delta H(A, l^0/s^0)}{RT^2} dT + x(B) \frac{\Delta H(B, l^0/s^0)}{RT^2} dT = -x(C) \cdot d \ln a(C) \quad (12)$$

Dependence of the activity of component C on concentration can be expressed by the universal relationship (12). Then we obtain

$$-x(C) \cdot d \ln (x(C))^k = -x(C) \cdot k \frac{dx(C)}{x(C)} = -k \cdot dx(C) \qquad (13)$$

where k is the number of new (foreign) species which one molecule of component C brings into the mixture $A + B$. Inserting from eqn (13) to eqn (12) we get after rearrangement

$$\mathrm{d}T = \frac{RT^2}{x(A) \cdot \Delta H(A, l^0/s^0) + x(B) \cdot \Delta H(B, l^0/s^0)} \cdot k \cdot \mathrm{d}x(C) \qquad (14)$$

In the limit for $x(C) \to 0$, $T \to T(E)$, $x(A) \to x(A, E)$, $x(B) \to x-(B, E)$, $\Delta H(i, l^0/s^0) \to \Delta H(i, E, l^0/s^0)$ and it holds

$$\lim_{x(C) \to 0} \frac{\mathrm{d}T}{\mathrm{d}x(C)} = -\frac{R(T(E))^2}{x(A, E) \cdot \Delta H(A, E, l^0/s^0) + x(B, E) \cdot \Delta H(B, E, l^0/s^0)} \cdot k \qquad (15)$$

When

$$x(A, E) \cdot \Delta H(A, E, l^0/s^0) + x(B, E) \cdot \Delta H(B, E, l^0/s^0) = \Delta H(\mathrm{fus}, A + B, E)$$

the derived relationship (15) is identical with the relationship (8) derived by *Haase* and *Schönert* [10].

Another possibility of derivation of the basic relationship for cryometry in ternary systems is based on the application of the isothermal-isobaric $\Delta G_{T,p}$ cycle.

Conditions for phase equilibria $A(l) \rightleftarrows A(s^0)$ (points E and E_1) and $B(l) \rightleftarrows B(s^0)$ (points E and E_2) at T, $p = \mathrm{const}$ (Fig. 2) are fulfilled if

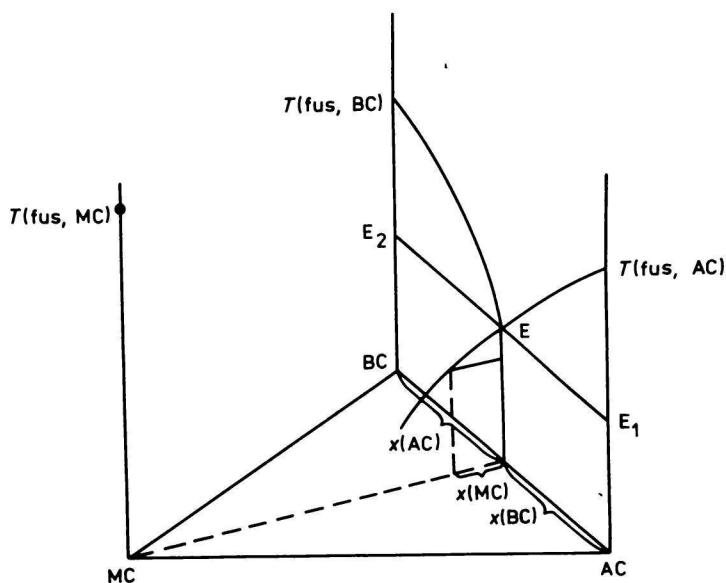$$\bar{G}(A, l) = G(A, s^0); \quad \bar{G}(B, l) = G(B, s^0)$$

Fig. 2. Scheme for derivation of the relations for cryometric method in ternary systems.

If we multiply the first condition by $x(A, E)$ and the second by $x(B, E)$ and add both terms we obtain

$$x(A, E) \cdot \bar{G}(A, l) + x(B, E) \cdot G(B, l) = x(A, E) \cdot G(A, s^0) +$$
$$+ x(B, E) \cdot G(B, s^0) \qquad (16)$$

Let us consider equilibrium at points Z and Z_1 (Fig. 2). In this case the components A, B in liquid phase composed of components $A + B + C$ are in equilibrium with pure solid components $A(s^0)$ and $B(s^0)$. We may choose as standard state an undercooled $(T < T(E))$ eutectic liquid solution of composition $x(A, E) + x(B, E)$. Then for the four-term $\Delta G_{T,p}$ cycle (Figs. 3a, 3b) it follows
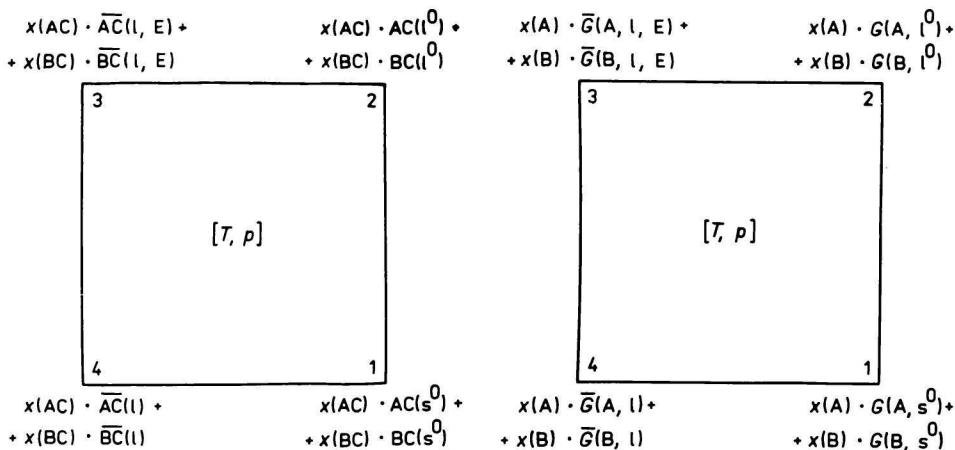
$$x(AC) \cdot \overline{AC}(l, E) + \qquad x(AC) \cdot AC(l^0) \cdot$$
$$+ x(BC) \cdot \overline{BC}(l, E) \qquad + x(BC) \cdot BC(l^0)$$

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3                          2
          [T, p]
4                          1
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$$x(AC) \cdot \overline{AC}(l) + \qquad x(AC) \cdot AC(s^0) +$$
$$+ x(BC) \cdot \overline{BC}(l) \qquad + x(BC) \cdot BC(s^0)$$

Fig. 3a. The isobaric-isothermal cycle.

$$x(A) \cdot \bar{G}(A, l, E) + \qquad x(A) \cdot G(A, l^0) +$$
$$+ x(B) \cdot \bar{G}(B, l, E) \qquad + x(B) \cdot G(B, l^0)$$

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3                          2
          [T, p]
4                          1
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$$x(A) \cdot \bar{G}(A, l) + \qquad x(A) \cdot G(A, s^0) +$$
$$+ x(B) \cdot \bar{G}(B, l) \qquad + x(B) \cdot G(B, s^0)$$

Fig. 3b. The isobaric-isothermal ΔG-cycle.

$$\Sigma \Delta G = \Delta G(2/1) + \Delta G(3/2) + \Delta G(4/3) + \Delta G(1/4) = 0$$

$$\Delta G(2/1) = x(A, E)(G(A, l^0) - G(A, s^0)) + x(B, E)(G(B, l^0) -$$
$$- G(B, s^0)) = x(A, E) \cdot \Delta G(A, l^0/s^0) + x(B, E) \cdot \Delta G(B, l^0/s^0)$$

$$\Delta G(3/2) = x(A, E) \cdot \Delta \bar{G}(A, (l, E)/l^0) + x(B, E) \cdot \Delta \bar{G}(B, (l, E)/l^0)$$

Index "l, E" denotes the undercooled liquid phase corresponding to composition of the point E.

$$\Delta G(4/3) = x(A, E) \cdot \Delta \bar{G}(A, l/(l, E)) + x(B, E) \cdot \Delta \bar{G}(B, l/(l, E))$$

Because $\Delta G(1/4) = 0$ (as a result of phase equilibrium) we obtain inserting into expression for $\Sigma\Delta G$ the equation

$$x(A, E) \cdot \Delta\bar{G}(A, l/(l, E)) + x(B, E) \cdot \Delta\bar{G}(B, l/(l, E)) =$$
$$= -[x(A, E) \cdot \Delta\bar{G}(A, (l, E)/s^0) + x(B, E) \cdot \Delta\bar{G}(B, (l, E)/s^0)] \qquad (17)$$

The term on the right-hand side of eqn (17) corresponds to the negative change in Gibbs energy of the process when 1 mol of mixture having composition $x(A, E)$, $x(B, E)$ melts and pure solid phases form liquid binary solution $A(l, E) + B(l, E)$; $x(A, E) + x(B, E) = 1$. Therefore the right-hand side of eqn (17) can be denoted as $\Delta G(\text{fus}, A + B, E)$. It holds

$$\Delta G(\text{fus}, A + B, E) = \Delta H(\text{fus}, A + B, E) - T \Delta S(\text{fus}, A + B, E)$$

and because

$$\Delta S(\text{fus}, A + B, E) = \Delta H(\text{fus}, A + B, E)/T(E)$$

we may further write

$$x(A, E) \cdot \Delta\bar{G}(A, l/(l, E)) + x(B, E) \cdot \Delta\bar{G}(B, l/(l, E)) =$$
$$= -\Delta H(\text{fus}, A + B, E) \left(1 - \frac{T}{T(E)}\right) \qquad (18)$$

Because the quantities $x(A, E)$, $x(B, E)$, $\Delta H(\text{fus}, A + B, E)$, $T(E)$ are constants derivation of eqn (18) according to $x(C)$ gives

$$x(A, E) \frac{d\Delta\bar{G}(A, l/(l, E))}{dx(C)} + x(B, E) \frac{d\Delta\bar{G}(B, l/(l, E))}{dx(C)} =$$
$$= \frac{\Delta H(\text{fus}, A + B, E)}{T(E)} \cdot \frac{dT}{dx(C)} \qquad (19)$$

Now we insert in the Gibbs—Duhem equation (10) for d ln $a(i)$, $(i = A, B)$, the expression $d\Delta\bar{G}(i, l/(l, E))/RT$ which can be obtained by derivation of the identity RT ln $a(i, l) = \bar{G}(i, l) - \bar{G}(i, (l, E)) = \Delta\bar{G}(i, l/(l, E))$.

After multiplying by the term $RT/dx(C)$ and rearrangement we obtain

$$x(A) \frac{d\Delta\bar{G}(A, l/(l, E))}{dx(C)} + x(B) \frac{d\Delta\bar{G}(B, l/(l, E))}{dx(C)} = -RTx(C) \cdot d \ln a(C) \qquad (20)$$

Let $a(C) = (x(C))^k$, then d ln $a(C) = d$ ln $(x(C))^k = k \cdot dx(C)/x(C)$ and after inserting to eqn (20) we obtain

$$x(A) \frac{d\Delta\bar{G}(l/(l, E))}{dx(C)} + x(B) \frac{d\Delta\bar{G}(B, l/(l, E))}{dx(C)} = RT \cdot k \qquad (21)$$

When $x(C) \to 0$, $x(A) \to x(A, E)$, $x(B) \to x(B, E)$ and it holds

$$\lim_{x(C) \to 0} \frac{\Delta H(\text{fus, A} + \text{B, E})}{T(E)} \cdot \frac{dT}{dx(C)} = -RT(E) \cdot k$$

or

$$\lim_{x(C) \to 0} \frac{dT}{dx(C)} = -\frac{R(T(E))^2}{\Delta H(\text{fus, A} + \text{B, E})} \cdot k \qquad (22)$$

Thus we obtained again eqn (8).

Finally it should be pointed out that a successfull realization of the cryometric method in ternary systems is not limited only to the systems with simple eutectic as it is stated in papers [9—11]. It is sufficient if the system A—B has a simple eutectic character and if no solid solutions are formed in the near vicinity of the curve of monovariant equilibrium starting at the point E.

Fellner and *Matiašovský* [11] found that in ideal systems the cryometry in the ternary systems can be correctly realized only if $\Delta H(\text{fus, A}) = \Delta H(\text{fus, B})$. This condition is too strict and it would mean a remarkable complication of the cryometric method. We try to eliminate these restrictions. The temperature dependence of the quantity $\Delta C_p(i)$ will be taken into account by employing the differential form of the Le Chatelier—Shreder equation

$$d \ln a(i) = \frac{\Delta H(i, l^0/s^0)}{RT^2} \, dT \qquad (23)$$

where $\Delta H(i, l^0/s^0) = H(i, l^0) - H(i, s^0)$ is the molar enthalpy corresponding to the phase transition "solidus—liquidus" of the pure i-th component at the temperature T. For $a(i) = x(i)$ it follows from eqn (23)

$$d \ln x(i) = \frac{dx(i)}{x(i)} = \frac{\Delta H(i, l^0/s^0)}{RT^2} \, dT \qquad (24)$$

For the $dx(A)/dx(B)$ we readily obtain

$$\frac{dx(A)}{dx(B)} = \frac{x(A) \cdot \Delta H(A, l^0/s^0)}{x(B) \cdot \Delta H(B, l^0/s^0)} \qquad (25)$$

Because $x(A)$, $x(B)$, and $x(C)$ are the mole fractions it holds

$$dx(C) = -dx(B) - dx(A)$$

and thus

$$\frac{dx(C)}{dx(B)} = -1 - \frac{dx(A)}{dx(B)} \qquad (26)$$

After introducing from eqn (25) into eqn (26) we obtain

$$\frac{dx(C)}{dx(B)} = -1 - \frac{x(A) \cdot \Delta H(A, 1^0/s^0)}{x(B) \cdot \Delta H(B, 1^0/s^0)}$$

and in the limit for $x(C) \to 0$

$$\lim_{x(C) \to 0} \frac{dx(C)}{dx(B)} = -1 - \frac{x(A, E) \cdot \Delta H(A, E, 1^0/s^0)}{x(B, E) \cdot \Delta H(B, E, 1^0/s^0)} \tag{27}$$

The index "E" at the quantities in eqn (27) denotes that these quantities are related to the eutectic point E in a simple binary system A—B (Fig. 4).

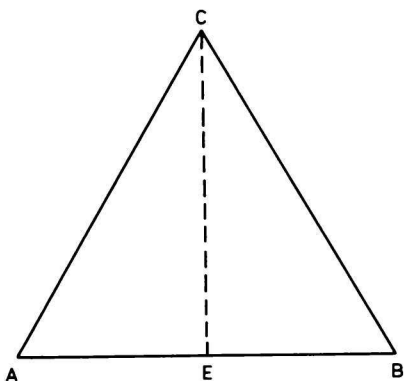For the equation of the line passing through the points C and E (Fig. 5) it holds

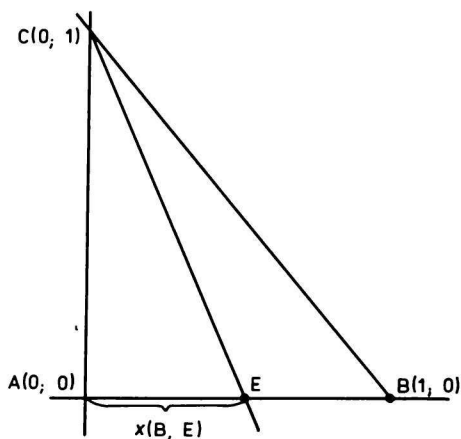Fig. 4. Cryometry in a ternary system based on the binary system A—B.

Fig. 5. The straight line connecting the points C and E.

$$x(C) = -\frac{1}{x(C, E)} x(B) + 1 \tag{28}$$

and further

$$\lim_{x(C) \to 0} \frac{dx(C)}{dx(B)} = -\frac{1}{x(B, E)} \tag{29}$$

Comparing eqns (27) and (29) we obtain that

$$-\frac{1}{x(B, E)} = -1 - \frac{x(A, E) \cdot \Delta H(1^0/s^0)}{x(B, E) \cdot \Delta H(1^0/s^0)} \tag{30}$$

Because $x(A, E) + x(B, E) = 1$ we can readily prove that eqn (30) is fulfilled only when

$$\Delta H(A, E, l^0/s^0) = \Delta H(B, E, l^0/s^0) \tag{31}$$

Eqn (31) is therefore a more precise condition for correctness of the cryometric method in the ternary systems with respect to the first limitation.

For nonideal systems it holds

$$d \ln a(i) = d \ln x(i) + d \ln \gamma(i)$$

and then

$$\frac{dx(i)}{x(i)} = \frac{\Delta H(i, l^0/s^0)}{RT^2} dT - d \ln \gamma(i) \tag{32}$$

Using the same procedure as above we find that it holds

$$\frac{1}{x(B, E)} = 1 + \frac{x(A, E) \, (\Delta H(A, E, l^0/s^0) \, dT - R(T(E))^2 \, d \ln \gamma(A, E))}{x(B, E) \, (\Delta H(B, E, l^0/s^0) \, dT - R(T(E))^2 \, d \ln \gamma(B, E))} \tag{33}$$

Thus for nonideal systems the condition $\Delta H(A, E, l^0/s^0) = \Delta H(B, E, l^0/s^0)$ does not hold.

In order to arrange eqn (33) in an explicit form we will assume that the activities of components A and B may be expressed by the universal relationship [12]

$$a(A) = (x(A))^{k(B/A)}$$
$$a(B) = (x(B))^{k(A/B)} \tag{34}$$

where $k(B/A)$, $k(A/B)$ equal the number of new (foreign) species which one molecule of substance B brings into substance A, and *vice versa*. In this case $d \ln a(i) = k(j/i) \, dx(i) x(i)$ and it holds

$$\frac{1}{x(B, E)} = 1 + \frac{x(A, E) \cdot \Delta H(A, E, l^0/s^0) \cdot k(A/B)}{x(B, E) \cdot \Delta H(B, E, l^0/s^0) \cdot k(B/A)} \tag{35}$$

From this we obtain the condition of correctness of cryometry

$$\Delta H(A, E, l^0/s^0) \cdot k(A/B) = \Delta H(B, E, l^0/s^0) \cdot k(B/A) \tag{36}$$

Eqn (36) is identical with the condition derived by Fellner and Matiašovský not only for $k(A/B) = 1$, $k(B/A) = 1$ but also for $k(A/B) = k(B/A)$.

From the formal point of view, the original condition $\Delta H(\text{fus}, A) = \Delta H(\text{fus}, B)$ (as well as the condition given by eqn (36)) is too stringent. If it held in that sense that a small difference between the quantities $\Delta H(\text{fus}, A)$ and $\Delta H(\text{fus}, B)$

(or more precisely between the terms $\Delta H(A, E, l^0/s^0) \cdot k(A/B)$ and $\Delta H(B, E, l^0/s^0) \cdot k(B/A)$) would lead to wrong values of the quantity $\Delta H(\text{fus}, A + B, E)$ it would mean a remarkable limitation of applicability of the cryometric method to investigation of the ternary systems.

We estimated the influence of the deviation from the given conditions on the quantity $\Delta H(\text{fus}, A + B, E)$ by means of the so-called theoretical experiment. The following procedure was used:

i) We chose for components A and B the following values of $T(\text{fus}, i)$ and $\Delta H(\text{fus}, i)$:

$$T(\text{fus, A}) = 1200 \text{ K}, \quad \Delta H(\text{fus, A}) = 30\ 000 \text{ J mol}^{-1}$$

$$T(\text{fus, B}) = 900 \text{ K}, 1200 \text{ K}, 2000 \text{ K}$$

$$\Delta H(\text{fus, B}) = 6000 \text{ J mol}^{-1}, 30\ 000 \text{ J mol}^{-1}, 60\ 000 \text{ J mol}^{-1}$$

ii) Using the Le Chatelier—Shreder equation we calculated the liquidus curves of components A and B in the binary system A—B up to 500 K (*i.e.* also for $T(i) < T(A + B, E)$). Their cross-section gives coordinates of the eutectic point in the system A—B. The calculations were carried out under the assumptions $\Delta H(\text{fus}, i) = \Delta H(i, l^0/s^0)$ and $a(i) = x(i)$.

iii) Formally the values $x(A) + x(B)$, $x(A, E) + x(B, E)$ give $T(i) < T(A + B, E)$ which is the decrease of temperature as a result of the addition of substance C. It must hold $x(A) + x(B) + x(C) = 1$.

iv) On the basis of known values of $x(A)$, $x(B)$, $x(C)$ the curves of monovariant equilibrium were constructed (Fig. 6).

v) For given $x(C)$ we determined ΔT and using the cryometric method we calculated $\Delta H(\text{fus}, A + B, E)$. The data used in the calculation according to the relationship

$$\Delta H(\text{fus, A + B, E}) = \frac{R(T(A + B, E))^2}{k(l^0)} \tag{37}$$

are summarized in Table 1.

The quantity $k(l^0)$ was determined by extrapolation of the dependence

$$\frac{\Delta T}{\Delta x(C)} = f(\Delta x(C))$$

from the condition $\Delta x(C) \to 0$.

vi) The values of $\Delta H(\text{fus}, A + B, E)$ calculated in this way were compared with ideal enthalpy of fusion of the system A—B at the eutectic point (Table 2)

$$\Delta H(A + B, E, \text{id}) = x(A) \cdot \Delta H(A, l^0/s^0) + x(B) \cdot \Delta H(B, l^0/s^0) \tag{38}$$

Table 1

The values $k(1^0)$ needed for the calculation of $\Delta H(\text{fus, A + B, E})$
$T(\text{fus, A}) = 1200 \text{ K}; \Delta H(\text{fus, A}) = 30\ 000 \text{ J mol}^{-1}$

$\dfrac{T(\text{fus, B})}{\text{K}}$	$\dfrac{\Delta H(\text{fus, B})}{\text{J mol}^{-1}}$		
	6 000	30 000	60 000
	$k(1^0)$	$k(1^0)$	$k(1^0)$
900	469	190	126
1200	470	260	210
2000	450	337	346

Table 2

Comparison of the values $\Delta H(\text{A + B, id, E})$ with the values $\Delta H(\text{fus, A + B, E})$, calculated under the application of cryometric method

$\dfrac{T(\text{fus, B})}{\text{K}}$	$\dfrac{\Delta H(\text{fus, B})}{\text{J mol}^{-1}} = 6\ 000$		
	$\Delta H(\text{fus, A + B, E})$	$\Delta H(\text{A + B, id, E})$	%
900	9 747.4	9 758.4	-0.1
1200	11 828.1	11 882.4	-0.5
2000	14 809.8	14 625.6	1.3

$\dfrac{T(\text{fus, B})}{\text{K}}$	$\dfrac{\Delta H(\text{fus, B})}{\text{J mol}^{-1}} = 30\ 000$		
	$\Delta H(\text{fus, A + B, E})$	$\Delta H(\text{A + B, id, E})$	%
900	30 502.9	30 000	1.7
1200	30 411.6	30 000	1.4
2000	30 048.2	30 000	1.4

$\dfrac{T(\text{fus, B})}{\text{K}}$	$\dfrac{\Delta H(\text{fus, B})}{\text{J mol}^{-1}} = 60\ 000$		
	$\Delta H(\text{fus, A + B, E})$	$\Delta H(\text{A + B, id, E})$	%
900	48 905.8	50 820.0	-3.8
1200	42 362.7	41 460.0	2.2
2000	32 832.5	32 307.0	1.6

From the condition given by eqn (36) it follows

$$\frac{\Delta H(A, E, l^0/s^0)}{\Delta H(B, E, l^0/s^0)} = \frac{k(B/A)}{k(A/B)}$$

The chosen ratio of enthalpies in examples corresponds to the ratio of correction factors 6 : 1 and it includes both the ideal systems and the systems the behaviour of
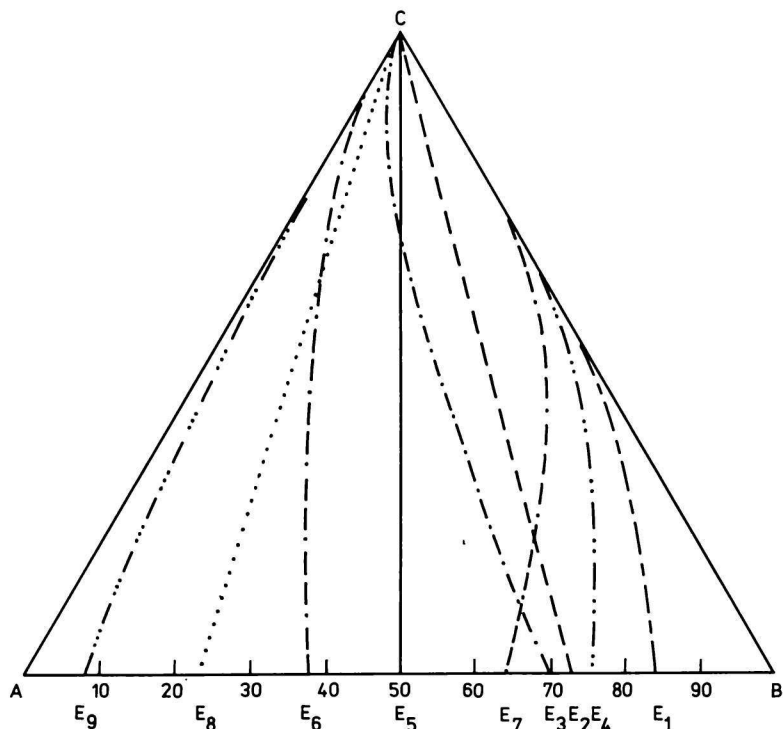

Fig. 6. The lines of monovariant equilibrium (of the common crystallization) of the substances A and B.

— · —	$T(\text{fus, B}) = 900$ K;	$\Delta H(\text{fus, B}) = 6\,000$ J mol^{-1}
— — —	$T(\text{fus, B}) = 900$ K;	$\Delta H(\text{fus, B}) = 30\,000$ J mol^{-1}
— · — · —	$T(\text{fus, B}) = 900$ K;	$\Delta H(\text{fus, B}) = 60\,000$ J mol^{-1}
— · · — · ·	$T(\text{fus, B}) = 1200$ K;	$\Delta H(\text{fus, B}) = 6\,000$ J mol^{-1}
———	$T(\text{fus, B}) = 1200$ K;	$\Delta H(\text{fus, B}) = 30\,000$ J mol^{-1}
— · —	$T(\text{fus, B}) = 1200$ K;	$\Delta H(\text{fus, B}) = 60\,000$ J mol^{-1}
— — · — —	$T(\text{fus, B}) = 2000$ K;	$\Delta H(\text{fus, B}) = 6\,000$ J mol^{-1}
· · · · · ·	$T(\text{fus, B}) = 2000$ K;	$\Delta H(\text{fus, B}) = 30\,000$ J mol^{-1}
— · · · —	$T(\text{fus, B}) = 2000$ K;	$\Delta H(\text{fus, B}) = 60\,000$ J mol^{-1}

which is very far from classical ideality. The temperature dependence of the phase transition $\Delta H(\text{i}, \text{l}^0/\text{s}^0)$ was not considered. However, this effect cannot exceed 30 % even for large temperature intervals and it is therefore included in the range of chosen values of $\Delta H(\text{fus}, \text{i})$.

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Translated by P. Fellner