

Cryometry in the eutectic mixtures

P. FELLNER and K. MATIAŠOVSKÝ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
809 34 Bratislava*

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The equations for the cryometry in the eutectic ideal systems were derived. Contrary to the generally accepted hypothesis it was found that this cannot be based on a relation analogous to Le Chatelier—Schröder's equation.

For the equilibrium solidus—liquidus of the component i in a simple eutectic system in which no compounds are formed and the solubility of the components in the solid state does not exist, the following relation holds

$$d \ln a_i = \frac{\Delta H_i^f}{RT^2} dT \quad (1)$$

(the differential form of Le Chatelier—Schröder's equation), where a_i and ΔH_i^f are the activity and the enthalpy of fusion, respectively, of the component i , T is the temperature, and R is the gas constant.

For simplification, it is assumed that $\Delta H_i^f \neq f(T)$ and further the solution is ideal, *i.e.* $a_i = x_i$. Then by integration and rearrangement of eqn (1), for the temperature depression of the primary crystallization of the component i the following relation is obtained

$$\Delta T = T_i^f - T = \frac{RT_i^f}{\Delta H_i^f} T(-\ln x_i), \quad (2)$$

where T_i^f and x_i are the temperature of fusion (melting point — m.p.) and the mole fraction, respectively, of the component i .

In a binary system A—B ($x_A + x_B = 1$) in the proximity of the m.p. of the pure component A ($x_A \approx 1$) it is approximatively valid that $-\ln x_A = -\ln(1 - x_B) \approx x_B$. Then, from eqn (2) for the m.p. depression of the substance A that was effected by minor additions of the substance B, the well-known relation is obtained

$$\Delta T = \frac{RT_A^f}{\Delta H_A^f} T x_B. \quad (3)$$

The problem arises whether it is possible to carry out analogous measurements also in the eutectic mixtures A—B, *i.e.* to determine the depression of the eutectic temperature effected by a minor addition of the substance C. For this case, *Førland* ([1], p. 105) derived an equation similar to eqn (3) by replacing T_A^f in eqn (3) by T_E^f (eutectic temperature), ΔH_A^f by ΔH_E^f (enthalpy of fusion of the eutectic mixture, which is independent of the concentration of the component C, x_C), and x_B by x_C . However, it will be shown that the equation proposed by *Førland* has not a general validity.

Let us consider an ideal ternary system A—B—C. In this case eqn (1) must hold for all three components. From the integral form of eqn (1) for the components A and B, the equation of a projection of the monovariant line of the simultaneous crystallization of these components, EP (Fig. 1) can be derived

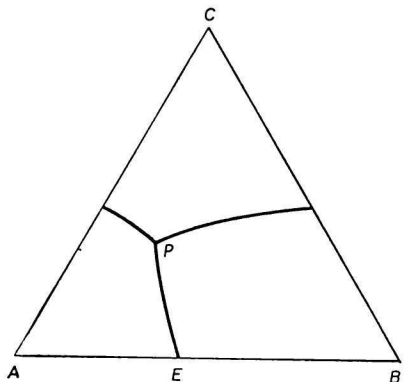


Fig. 1. The phase diagram of the ternary system A—B—C in which no solid solutions are formed.

$$\frac{\ln x_A}{\Delta H_A^f} - \frac{\ln x_B}{\Delta H_B^f} = \frac{1}{R} \left(\frac{1}{T_A^f} - \frac{1}{T_B^f} \right). \quad (4)$$

The eutectic concentration of the components A and B will be denoted as x_A^+ and x_B^+ . In eqn (4), the temperature is not expressed explicitly; it can be calculated by introducing eqn (4) into the integral form of eqn (1) for the components A and B, respectively.

As mentioned above, Førland's equation for the depression of the eutectic temperature [1] is based on the assumption that $\Delta H_E^f = \text{const}$. Thus assuming the relation $\Delta H_E^f = x_A^+ \Delta H_A^f + x_B^+ \Delta H_B^f$, the ratio of x_A and x_B on the monovariant line of the simultaneous crystallization of A and B should be also constant, *i.e.* it must not be a function of x_C . However, this condition is satisfied only on the assumption that the monovariant line EP is, at least in the proximity of the binary eutectic point E, identical with the connecting line EC. The diagram presented in ([1], p. 104) for illustration of the proposed relation was drawn in such a way that it might fulfil the above condition. However, in a common case, the slope of the tangent to the line of the simultaneous crystallization of the components A and B can be calculated after substituting for A in eqn (4) the expression $x_A = 1 - x_B - x_C$ by differentiating eqn (4) as an implicit function

$$\frac{dx_C}{dx_B} = -1 - \frac{x_A \Delta H_A^f}{x_B \Delta H_B^f}. \quad (5)$$

Eqn (5) can be derived also directly from the differential form of eqn (1). The slope of the connecting line EC in oblique-angled coordinates equals $-1/x_B^+$, whereas according to eqn (5) for this slope we obtain

$$\lim_{x_C \rightarrow 0} \frac{dx_C}{dx_B} = -1 - \frac{x_A^+ \Delta H_A^f}{x_B^+ \Delta H_B^f}. \quad (6)$$

This limit equals $-1/x_B^+$ solely in case $\Delta H_A^f = \Delta H_B^f$. Only in this case the ratio x_A/x_B in an ideal system is constant and equal to the ratio x_A^+/x_B^+ . Consequently, the statement that the ratio x_A/x_B is constant implies the condition that the enthalpies of fusion of both components which compose the eutectic mixture are equal.

Setting $i = B$ from eqn (5) into eqn (1), the relation is obtained

$$dT = - \frac{RT^2}{x_A \Delta H_A^f + x_B \Delta H_B^f} dx_C, \quad (7)$$

which actually appears to be the differential form of the equation of the line of the simultaneous crystallization of the components A and B. This equation may be derived also directly from eqn (1). From a comparison of eqns (7) and (1) it follows that in eqn (7) the increase in the concentration of the component C is presented as dx_C and not as $d \ln x_C$. Only if $\Delta H_A^f = \Delta H_B^f$, by rearranging eqn (7) the relation is obtained

$$dT = \frac{RT^2}{\Delta H_A^f (x_A + x_B)} d(x_A + x_B) = \frac{RT^2}{\Delta H_A^f} d \ln (x_A + x_B). \quad (8)$$

In a limiting case for $x_C \rightarrow 0$, from eqn (7) it follows:

$$\lim_{x_C \rightarrow 0} \frac{dT}{dx_C} = - \frac{RT_E^2}{x_A^+ \Delta H_A^f + x_B^+ \Delta H_B^f}. \quad (9)$$

Thus the cryometric measurements may be performed also in the eutectic mixtures

since the value of the $\lim_{x_C \rightarrow 0} \frac{dT}{dx_C}$ can be determined. However, it is to be taken into

consideration that the reasons, why the function $\Delta T = f(x_C)$ is not linear, are in this case somewhat different. This difference must be considered in the experimental work, namely in the estimation of the maximal value of x_C at which the error in the determination of temperature resulting from the non-constant value of the denominator in eqn (7) still lies below the limit of the experimental determinability.

In a common case, in the calculation of the enthalpy of fusion of an eutectic mixture evidently also the temperature dependence of ΔH_A^f and ΔH_B^f , as well as the enthalpy of mixing of these components must be considered. This, however, does not affect the principal meaning of the above-derived dependences.

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