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CRYOSCOPY OF REAL SOLUTIONS

B. KAWALEC

Institute of Physical Chemistry of the Polish Academy of Sciences, 01—224 Warsaw, Poland

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A new equation of the cryoscopic curve has been derived. This equation relates the equilibrium temperature of the solution, T, to sample mole fraction, F, melted at T:

$$T = T^0_{m_i} - \frac{R(T^0_{m_i})^2/\Delta H^0_{m_i}}{F/x_j + 2a(1-F)}$$

This equation takes into account the effect of departure of solutions from ideality and solubility of their components in the solid phase.

The data obtained indicate that an accuracy to within 10% of the actual impurity values can be anticipated in the 98 to 99.9% purity range.

The equation of the cryoscopic curve which relates the equilibrium temperature of the solution to sample mole fraction melted at this temperature, has the following form [1]

$$T = T^0_{m_i} - \frac{R(T^0_{m_i})^2}{\Delta H^0_{m_i}} \cdot x_j \cdot \frac{1}{F} \tag{1}$$

where $T^0_{m_i}$, $\Delta H^0_{m_i}$, R and x_j are constants.

A plot of T vs. $1/F$ should be a straight line of slope $-R(T^0_{m_i})^2 x_j/\Delta H^0_{m_i}$ and intercept $T^0_{m_i}$.

Knowledge of the molar enthalpy of melting of the solvent permits, for instance, calculation of the solute content in the solution. Many other properties of the solution can be calculated, too.

Equation (1) is an approximation and can be expected to hold for solutions that are closely related to ideal and whose components are totally insoluble in the solid phase (simple eutectic systems). Such systems are not met in practice [2]. For this reason, experimental data (T vs. $1/F$) obtained by means of both static [3] and dynamic methods almost always form a curve and can hardly be considered to be even in qualitative agreement with Eq. (1).

Much research has been done in order to elucidate the reasons why the investigated sample does not "obey" Eq. (1) perfectly.

Considering variants of phase diagrams (Fig. 1), one may conclude that a positive departure from ideality (a general case in organic systems) changes the phase diagram from a continuous series of liquid and solid solutions to the eutectic type, whereas solubility of the components in the solid phase increases in the reverse order [2].

Mastrangelo [4] and Smit [5] developed equations which assume equilibrium conditions of freezing (rarely realized in practice) [6] and ideal liquid and solid solubility of the components:

$$T = T^0_{m_i} - \frac{R(T^0_{m_i})^2}{\Delta H^0_{m_i}} \cdot x_j \cdot \frac{1}{\frac{k}{(1-k)} + F} \tag{2}$$

It appears that the Mastrangelo and Smit approaches are limited to systems which exhibit complete solubility of the components in both the liquid and solid states (Fig. 1a). In practice such solutions are only rarely met with.

Smit [7] and Lashkevich [8] developed another equation which assumes complete mixing conditions in the liquid [6], complete fractionation conditions in the solid [9], and no departure from ideality in either the liquid or solid

$$T = T^0_{m_i} - \frac{\Delta(T^0_{m_i})^2}{\Delta H^0_{m_i}} \cdot x_j \cdot \frac{(1-k)}{F^{(1-k)}} \tag{3}$$

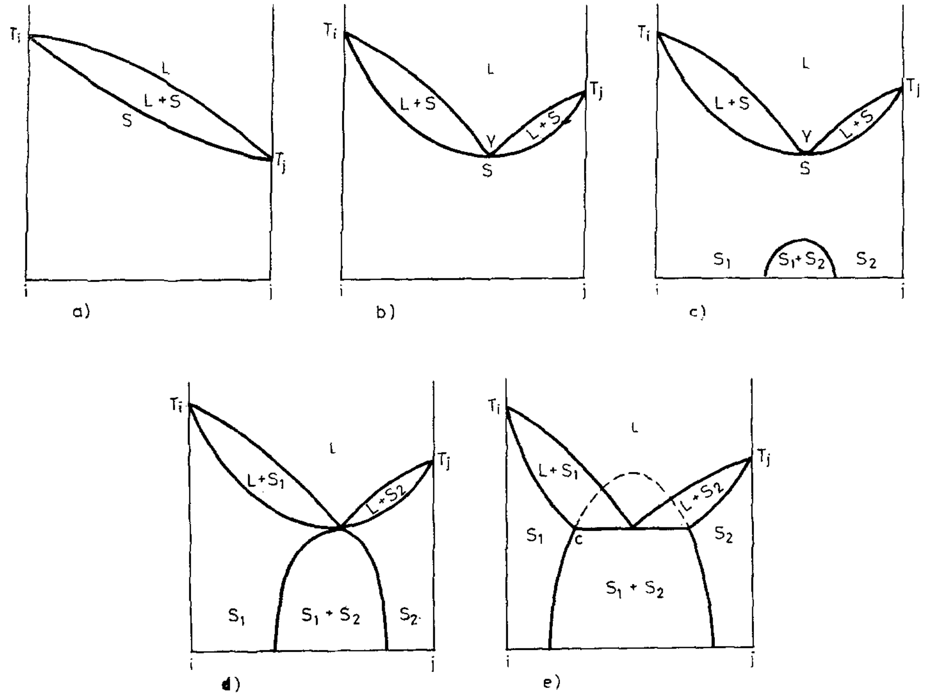

Fig. 1. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solid solutions to a eutectic type

This approach is also limited to systems which exhibit complete solubility in the liquid and solid.

Badley discusses a treatment of cryoscopic data when the liquid phase is non-ideal [10]. Departure from ideality in the liquid phase has less influence on the cryoscopic data than that in the solid phase.

The purpose of the present work is to derive a new equation for a binary system, which would take into account the effect of departure of liquid and especially solid solutions from ideality, solubility of their components in the solid phase, and segregation in the solid. This equation should be applicable to systems which exhibit both complete and limited solubility of the components in the solid phase. These systems are generally met in practice.

Methods of calculation

It is assumed that

1. the liquid and especially solid solutions are diluted real solutions and the activity coefficients of components are given by expressions of the regular type (reference state – infinitely diluted liquid or solid solution) [11];
2. the solubility of one component in another may be so low that it is difficult to detect experimentally, but there will always be a measure of solubility in the solid phase;
3. freezing is slow enough for mixing to erase all concentration gradients in the liquid (complete mixing conditions of freezing), but fast enough so that diffusion rates in the solid are negligible. The non-uniform solid phase has a zoned or otherwise cored structure. Crystal layers that have formed one upon another insulate the main crystal mass from the liquid. Thus, the liquid – insulating crystal layer system may be considered to be in equilibrium and the notion of equilibrium is still applicable. The remaining part of the crystal mass is treated as failing to participate in the crystallization process (complete fractionation conditions of freezing).

Consider a solid phase in equilibrium with its melt. By the condition of equilibrium for the solvent we obtain

$$\frac{\mu_i^{\mathrm{st.L}} - \mu_i^{\mathrm{st.S}}}{RT} = \ln a_i^{\mathrm{S}} - \ln a_i^{\mathrm{L}} \tag{4}$$

Further, considering the temperature-dependence of Eq. (4) we obtain

$$\frac{\Delta H_{\mathrm{m_i}}^0}{RT^2}\,\mathrm{d}T = \mathrm{d}\ln a_i^{\mathrm{L}} - \mathrm{d}\ln a_i^{\mathrm{S}} \tag{5}$$

According to the first assumption the activities in Eq. (5) are given by expressions of the regular type

$$\ln a_i^{\mathrm{L}} = A(x_j^{\mathrm{L}})^2 + \ln x_i^{\mathrm{L}} \tag{6}$$

$$\ln a_i^{\mathrm{S}} = B(x_j^{\mathrm{S}})^2 + \ln x_i^{\mathrm{S}} \tag{7}$$

By introducing into (6) and (7) the following approximation: $\ln x_i = \ln(1 - x_j) \cong \cong - x_j$, which may be expected to hold for diluted solutions, we obtain

$$\ln a_i^L = A(x_j^L)^2 - x_j^L \tag{8}$$

$$\ln a_i^S = B(x_j^S)^2 - x_j^S \tag{9}$$

In (5), $\ln a_i^L$ and $\ln a_i^S$ may be replaced by the right-hand sides of Eqs (8) and (9) Thus, we obtain

$$\frac{\Delta H_{m_i}^0}{RT^2} dT = 2Ax_j^L \cdot dx_j^L - dx_j^L - 2Bx_j^S \cdot dx_j^S + dx_j^S \tag{10}$$

Unlike ideal solutions, in diluted real solutions the solute content in the solid is not a linear function of the solute content in the liquid. In order to relate the solute content in the solid to its content in the liquid, it is assumed (assumption 2) that

$$x_j^S = a(x_j^L)^2 \tag{11}$$

The parameter a of this important equation depends on both the solubility in the solid and departure from ideality of the investigated solution. Eq. (11) cannot be ruled out by a thorough thermodynamic analysis.

Substituting Eq. (11) into (10) and neglecting all terms except for the zero and first-order terms, we obtain

$$\frac{\Delta H_{m_i}^0}{RT^2} dT = 2(A + a)\, x_j^L \cdot dx_j^L - dx_j^L \tag{12}$$

Integrating Eq. (12) with respect to temperature over the range $T_{m_i}^0$ to T, and with respect to composition over the range 0 to x_j^L, and putting $T_{m_i}^0 T \cong (T_{m_i}^0)^2$, we obtain

$$\frac{\Delta H_{m_i}^0}{R(T_{m_i}^0)^2} (T_{m_i}^0 - T) = x_j^L - (A + a)\,(x_j^L)^2 \tag{13}$$

Eq. (13) relates the composition of a diluted real solution to its equilibrium temperature.

The above description assumes (assumption 3) that complete mixing conditions in the liquid and complete fractionation conditions in the solid are maintained at all stages of the crystallization process. Therefore, the composition of the last solid to separate is not equal to the average composition of the solid but is equal to the composition that corresponds to the equilibrium with the liquid [12, 13]:

$$x_j^S = \frac{dp}{dz} \tag{14}$$

Of course, the composition of the liquid at all stages of the crystallization process is equal to the average composition of the liquid:

$$x_j^L = \frac{p}{z} \tag{15}$$

According to Eq. (11) the ratio x_j^S/x_j^L is a linear function of x_j^L in the region where the solution is diluted. Thus, Eq. (14) may be rewritten in the following form:

$$x_j^S = \frac{dp}{dz} = \frac{x_j^S}{x_j^L} \cdot \frac{p}{z} = ax_j^L \cdot \frac{p}{z} \tag{16}$$

Separating variables and putting $p = zx_j^L$ we obtain

$$\frac{dz}{z} = \frac{dx_j^L}{x_j^L(ax_j^L - 1)} \tag{17}$$

Eq. (17) may be integrated with respect to the mass of the liquid over the range z_0 to z and with respect to composition over the range x_j to x_j^L. After rearrangement we obtain

$$z/z_0 = \frac{(ax_j^L - 1)\, x_j}{(ax_j - 1)\, x_j^L} \tag{18}$$

Because the left-hand side of Eq. (18) is equal to F, it may be rewritten in the following form

$$x_j^L = \frac{1}{F/x_j + a(1 - F)} \tag{19}$$

When $F \to 0$, then $x_j^L \to x_j^S$ (see Eq. 11). This is in agreement with the well-known facts that

- if a system which forms a continuous series of liquid and solid solutions is cooled under conditions of complete fractionation, it will always reach the lowest point of the liquidus curve, i.e. the last remaining part of the melt is the pure component;
- under equilibrium conditions of cooling, systems with compositions between (c) and (T_i) (Fig. 1c) do not undergo the eutectic reaction since the liquid never reaches the eutectic composition. In the case of complete mixing conditions of the liquid and complete fractionation of the solid, the liquid will often reach the eutectic point although the composition of the solution is to the left of point (c). The quantity of liquid at the eutectic point is generally small.

Substituting (19) into (13), rearranging and putting $(x_j)^2 = 0$ since the solute content in the solutions investigated by means of cryoscopy is always less than 1 mole %, we obtain

$$T = T_{m_i}^0 - \frac{R(T_{mi}^0)^2/\Delta H_{m_i}^0}{F/x_j + 2a(1 - F)} \tag{20}$$

Eq. (20) relates the equilibrium temperature of the solution to sample mole fraction melted at this temperature.

Eqs (20) and (1) become identical when $a = 0$, i.e. when the solution is ideal and there is no solubility in the solid.

The influence of the parameter a on Eq. (20) is quite different from the influence of the parameter k on Eq. (2) given by Mastrangelo. Inasmuch as in Mastrangelo's equation its influence is expressed by a term $k/1 - k$ independent of other factors, then in Eq. (20) its influence is more complicated and depends on the composition of the solution. If x_j decreases, the weight of the $2a(l - F)$ term in the denominator of Eq. (20) becomes less and Eq. (20) approaches Eq. (1). For this reason, cryoscopic curves of very diluted solutions are linear if plotted as T vs. l/F.

Let us analyse the above statement in more detail by means of Eqs (13), (11) and (10). An important feature of Eq. (13) is that T vs. x_j^L is concave (if A is positive) and has a finite slope as x_j^L approaches zero

$$\frac{dT}{dx_j^L} - \frac{R(T_{m_i}^0)^2}{\Delta H_{m_i}^0} \quad \text{and} \quad \frac{d^2T}{d(x_j^L)^2} > 0 \quad \text{as} \quad x_j^L \to 0 \tag{21}$$

The concavity of the T vs. x_j^L line is characteristic only in a limited range of x_j^L and results from approximations that have been made while obtaining Eq. (13). If this is not the case, Eq. (10) rather than Eq. (13) should be used for a similar analysis. A second differentiation of Eq. (10) with respect to x_j^L gives

$$\frac{d^2T}{d(x_j^L)^2} = \frac{RT^2}{\Delta H_{m_i}^0}[2(A + a) - 12Ba^2(x_j^L)^2] \tag{22}$$

Thus, if x_j^L increases, the $12Ba^2(x_j^L)^2$ term will increase and the initially concave T vs. x_j^L line becomes convex, as frequently observed in practice [14 – 16].

Substituting Eq. (11) into (13), we obtain

$$T = T_m^0 - a^{-1/2}\frac{R(T_{m_i}^0)^2}{\Delta H_{m_i}^0}(x_j^S)^{1/2} + (A/a + 1)\frac{R(T_{m_i}^0)^2}{\Delta H_{m_i}}x_j^S \tag{23}$$

An important feature of Eq. (23) is that T vs. x_j^S is concave and has an infinite slope as x_j^S approaches zero

$$\frac{dT}{dx_j^S} \to \infty \quad \text{and} \quad \frac{d^2T}{d(x_j^S)^2} > 0 \quad \text{as} \quad x_j^S \to 0 \tag{24}$$

Analysis of the first and second derivatives shows that the solidus curve is very close to the ordinate of the phase diagram and that the solubility of one component in another may be so low that it is difficult to detect experimentally, but there will always be a measure of solubility. Consequently, a system which exhibits limited solubility in the solid phase behaves as a simple eutectic system when very diluted.

Eq. (20) may be rearranged to yield [17]

$$(T_{m_i}^0 - T)^{-1} = (1/x_j - 2a)\frac{\Delta H_{m_i}^0}{R(T_{m_i}^0)^2} \cdot F + 2a\frac{\Delta H_{m_i}^0}{R(T_m^0)^2} \tag{25}$$

There are two unknown quantities in Eq. (25): x_j and $T_{m_i}^0 \cdot T_{m_i}^0$ may be evaluated by the trial-and-error procedure until the assumed straight line of the plot $(T_{m_i}^0 - T)^{-1}$ vs. F is achieved. The slope of this line will be $(1/x_j - 2a)\Delta H_{m_i}^0/R(T_m^0)^2$ and the intercept $2a\Delta H_m^0/R(T_{m_i})^2$. Thus, if $\Delta H_{m_i}^0$ is known we are able to calculate x_j.

Experimental and results

The following systems have been investigated: benzene, benzene + 0.34mole % thiophene, and benzene + 0.77 mole % *n*-heptane. In these systems the departure from ideality increases from the benzene – thiophene to the benzene – *n*-heptane system, whereas solubility of the components in the solid phase increases in the reverse order.

The apparatus for melting curve measurements and the procedure for evaluating F have been described by Kawalec and Malanowski [18].

The results on purity determination are presented graphically in Fig. 2 in the form of T vs. $1/F$. It is seen that these data can hardly be considered to be even in qualitative agreement with Eq. (1)

Afterwards these data were recalculated according to Eq. (25). $T^0_{\mathrm{m_i}}$ was found equal to 279.16 K. The results are presented graphically in Fig. 3, in the form of

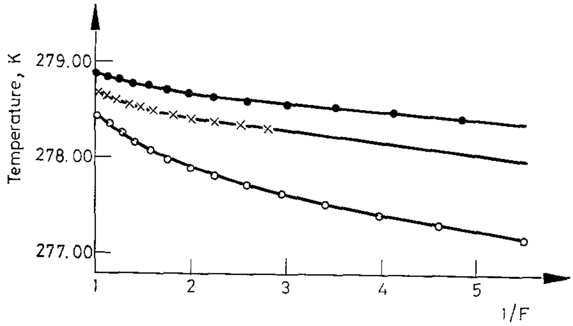

Fig. 2. Cryoscopic curves of benzene (●), benzene + 0.34 mole % thiophene (×), and benzene + 0.77 mole % *n*-heptane (o)

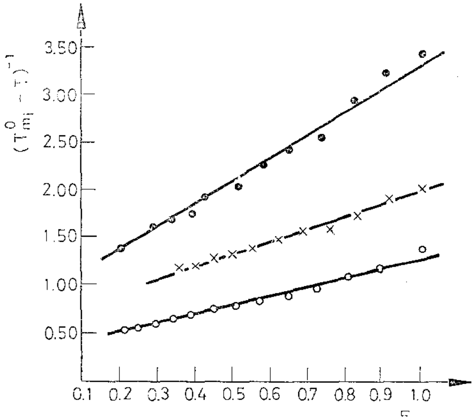

Fig. 3. Cryoscopic curves of benzene (●), benzene + 0.34 mole % thiophene (×), and benzene + 0.77 mole % *n*-heptane (o)

$(T^0_{m_i} - T)^{-1}$ vs. F. These data form approximately a straight line and are in good agrement with Eq. (25), which means that the assumptions made are reliable if the experiment is valid.

Estimates of the accuracy of the purity evaluations are presented in Table 1. The data from Table 1 indicate that an accuracy to within 10% of the actual impurity can be anticipated in the 98 to 99.9% purity range.

Table 1

Summary of the benzene purity results. Major componet—benzene
Impurity—thiophene and *n*-heptane

Physical property Solution	T_{m_i}	T	Impurity added, mole%	Total impurity, mole%	Exp. impurity, mole%	Relative error, %
Benzene	279.16	278.87	0.00	0.46[1]	0.46	—
Benzene — thiophene	279.16	278.67	0.34	0.80	0.78	2.6
Benzene — *n*-heptane	279.16	278.44	0.77	1.23	1.15	6.9

[1] Experimentally determined

Because the benzene had been carefully purified the high impurity content of the initial sample has to be noticed. This is probably due to the fact that more reliable assumptions have been made while developing Eq. (20). Another reason arises from the fact that the whole experimental T, F curve has been used for purity determination and the lack of thermal equilibrium has not been considered in the present paper. Driscoll et al., who examined the methods for purity measurement by DSC, found that the calculated impurity varies considerably with the F limits used [19].

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Symbols

T – equilibrium temperature of the liquid with its solid, K
$T^0_{m_i}$ – melting temperature of the solvent, K
x_j – solute content in the solution, mole fraction
x_j^L, x_j^S – solute contents in the liquid and solid phase, respectively, mole fraction

x_i^L, x_i^S – solvent contents in the liquid and solid phase, respectively, mole fraction
F – fraction melted
$\mu_i^{st.L}$, $\mu_i^{st.S}$ – partial molar standard chemical potentials of the solvent in the liquid and solid phase, respectively, cal. mole^{-1}
a_i^L, a_i^S – activities of the solvent in the liquid and solid phase, respectively
A, B – constants of Eqs (4) and (5), respectively, cal · mole^{-1}
$\Delta H_{m_i}^0$ – molar enthalpy of melting of the solvent, cal · mole^{-1}
R – gas constant, cal · deg^{-1} · mole^{-1}
k – partition coefficient, dimensionless
a – parameter of Eq. (11), dimensionless
p – mass of solute in the liquid phase, mole
z, z_0 – mass of liquid at the given moment and at the initial moment of crystallization, respectively, mole

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Résumé — On établit une nouvelle équation pour la courbe cryoscopique. Cette équation relie la température d'équilibre T de la solution et la fraction molaire F, fondue, à la température T:

$$T = T_{m_i}^0 - \frac{R(T_{m_i}^0)^2/\Delta H_m^0}{F/x_j + 2a(1 - F)}$$

Cette relation tient compte de l'écart des solutions à l'état idéal et de la solubilité de leurs constituants dans la phase solide.

Les données obtenues montrent qu'on peut compter sur une exactitude de 10% par rapport à la valeur réelle de l'impureté, dans le domaine de pureté allant de 98 à 99.9%.

ZUSAMMENFASSUNG — Es wurde eine neue Gleichung für die kryoskopische Kurve abgeleitet. Diese Gleichung beschreibt die Beziehung zwischen der Gleichgewichts temperatur der Lösung T und der Molfraktion der Probe F, geschmolzen bei T:

$$T = T^0_{\mathrm{m_j}} - \frac{R(T^0_{\mathrm{m_j}})^2/\Delta H^0_{\mathrm{m_i}}}{F/x_{\mathrm{j}} + 2a(1 - F)}.$$

Die Gleichung berücksichtigt die Abweichung der Lösungen vom Idealzustand und die Löslichkeit ihrer Komponenten in der festen Phase.

Die erhaltenen Datenweisen darauf hin, dass mit einer Genauigkeit innerhalb 10% des vorliegenden Verunreinigungswertes im Reinheitsbereich von 98 bis 99.9% zu rechnen ist.

Резюме — Было выведено новое уравнение криоскопической кривой, которое связывает равновесную температуру раствора, T, и мольную долю образца, F, плавящегося при T:

$$T = T^0_{\mathrm{m}} - \frac{R(T^0_{\mathrm{m}})^2/\Delta H^0_{\mathrm{m}}}{F/x_{\mathrm{j}} + 2a(1 - F)}$$

Представленное уравнение учитывает влияние отклонений растворов от идеальных и растворимость их компонентов в твердой фазе. Полученные данные показывают, что точность в пределах 10% действительного значения примеси можно предвидеть для области чистоты от 98 до 99,9%.