10

Calculation of the Fusibility Diagrams of Quasi-Simple Ternary Systems Model (QSTSM). Algorithm and Thermodynamic Justification

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This paper presents a model-free algorithm for calculating the melting diagrams of multicomponent quasi-simple systems from data on the melting diagrams of binary components. A proof is given that all invariant points of quasi-simple ternary systems belong to a single monovariant curve, and systems of equations for calculating this curve are presented. A system of transcendental equations is compiled for calculating the temperatures of ternary eutectics from data on the binary eutectics of quasi-simple subsystems. A thermodynamic method is proposed for determining whether a multicomponent system belongs to the class of quasi-simple systems solely from data on the coordinates of binary eutectics. The proposed algorithm is applicable to the thermodynamic calculation of any phase diagrams, including systems containing water-soluble nanoclusters.

Keywords: quasi-simple multicomponent systems, rectilinear liquidus isotherms, melting diagrams, non-model calculation, binary subsystems.

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1. Introduction

Almost all multicomponent systems involving carbon nanoclusters are nanostructured. These are fullerenes and their derivatives, graphenes and their derivatives, modified nanodiamonds. These systems are quasi-spaces: with direct isotherms-isobars-isopotentials of solvent (water). Phase diagrams with their participation are described according to the thermodynamic algorithm presented in this paper. Unfortunately, direct experimental data on phase equilibria in such nanosystems are not found in the literature. This paper provides an example of calculating the phase diagram of a quasi-simple nanosystem in comparison with experimental data.

2. Properties of quasi-simple systems

We will call a quasi-simple three- or more component system ($n \geq 3$) if the isotherms-isobars-isopotentials of the component of the system are straight line segments ($n = 3$), sectors of planes ($n = 4$) or hyperplanes ($n \geq 5$) (isopotentials of the i-th component — the geometric location of the figurative points of compositions with a constant value of the chemical potential $\mu_i = (\partial G/\partial n_i)_{T,P,n_{j \neq i}}$). We point out that practically all systems containing water-soluble nanoclusters and water as a solvent are in reality quasi-simple, with direct isopotentials of water. The study of special properties of this type of system has almost a century-long history [1–10]. At the same time, historically, the authors of such reviews have used double terminology.

A) When describing isothermal-isobaric solubility diagrams, systems with rectilinear solvent isopotentials (usually water — W) are called „obeying the Zdanovsky rule“ [1–8]. In this case, the isopotentials of other components are always curved (for example [7,8]).

Mathematically, the latter means for a triple system:

$$\left.\frac{m_1}{m_1^0}\right|_{\mu_w} + \left.\frac{m_2}{m_2^0}\right|_{\mu_w} = 1, \tag{1}$$

where m_i and m_i^0 are the molalities of the i-th component in a triple and binary solution with one value of the chemical potential of water — μ_w or the activity of water — a_w, respectively ($\mu_w = \mu_W^{(0)}(T, P) + RT \ln a_w$). In the case of an n-component system, the equation of the isoactive hyperplane has the form:

$$\sum_{i=1, i \neq w}^{n-1} \left.\frac{m_i}{m_i^0}\right|_{\mu_w} = 1. \tag{2}$$

B) Quasi-simple systems are also found in the description of polythermal-isobaric melting diagrams of a system with rectilinear liquidus isotherms (the latter — geometric location of figurative points of compositions with a constant value $T^{(l)}$ — temperatures of the appearance of the first crystals upon cooling homogeneous melts). If a similar straightness is observed in the crystallization field of the i-th component, then the liquidus isotherm is the isotherm-isobar-isopotential of the i-th component of the system. According to the terminology of the school of A. Storonkin [9–12] such systems are called „pseudo-ideal". Thus, when considering liquidus isotherms in the field of crystallization of an individual component, both concepts of A) and B) are identical. At the same time (since all components of the melt are equal), isotherms-isobars-isopotentials in the fields of other $j, k \neq i$ individual components of the system, as a rule, are also rectilinear. Mathematically, the latter means for a triple system:

$$\left.\frac{X_1}{X_1^0}\right|_{T^{(l)}} + \left.\frac{X_2}{X_2^0}\right|_{T^{(l)}} = 1, \tag{3}$$

where X_i and X_i^0 are the molar fractions of the i-th component in the ternary and binary systems, respectively, with equal value of the liquidus isotherms — $T^{(l)}$. In the case of a n-component system, the equation of the isoactive hyperplane has the form:

$$\sum_{i=1}^{n-1} \left.\frac{X_i}{X_i^0}\right|_{T^{(l)}} = 1. \tag{4}$$

It is quite clear that expressions (1), (2) and (3), (4) express the same linear relationship between the numbers of moles of all components of the liquid phase — n_i.

3. Justification of the basic formula of non-model calculation

We adapt the thermodynamic description of quasi-simple systems, given in Refs. [7,8] to quasi-simple melting diagrams. Let us consider n-component melt of the composition (X^{mult}, formed by mixing n binary melts of the composition (X_i^{bin}, taken at the same temperature T, and when mixed, the temperature of the triple solution has not changed. It was shown in Refs. [7,8] that the change in the Gibbs potential during the formation of a quasi-simple multicomponent melt (G_{mix}) is determined only by the entropy of ideal mixing of binary melts at a given temperature (considered as quasi-components of a multicomponent system):

$$G_{\mathrm{mix}}/RT = \sum_{i=2}^{n} Z_i \ln Z_i = \sum_{i=2}^{n} Z_i \ln(\ln a_i^{mult} - \ln a_i^{bin}), \tag{5}$$

where a_i^{mult}, a_i^{bin} is the activity of the i-th component in a multicomponent and binary melt $(1-i)$ of the same temperature, respectively, Z_i is an analog of the Yenecke index on solubility diagrams [7,8], and we keep the notation:

$$Z_i = \frac{X_i^{mult}}{X_i^{bin}}, \quad \sum_{i=1}^{n} Z_i = 1. \tag{6}$$

It follows directly from the equations (5) that:

$$\ln X_i^{mult} - \ln X_i^{bin} = \ln a_i^{mult} - \ln a_i^{bin}, \tag{7}$$

which we will call the equation of quasi-simple systems.

Let us now consider the triple system (index $(ter = i - j - k)$), namely, the branch of joint crystallization of components $(i-j)$ starting from a binary non-invariant point — eutectic with coordinates: (T_{ij}^{eut}; $X_i^{eut} = 1-X_j^{eut}$). Let's apply the basic equation (7) to a triple melt of composition X_i^{ter} at a temperature of T and a eutectic binary melt of composition X_i^{bin} (here and everywhere else, the index „*eut*" corresponds to eutectic melts):

$$\begin{aligned} \ln X_i^{ter} - \ln X_i^{bin} &= \ln a_i^{ter} - \ln a_i^{ter}, \\ \ln X_i^{eut} - \ln X_i^{bin} &= \ln a_i^{eut} - \ln a_i^{ter}. \end{aligned} \tag{8}$$

Applying the reasoning to both components, we get:

$$\begin{aligned} \ln X_i^{ter} &= \ln X_i^{eut} + \ln a_i^{ter} - \ln a_i^{eut}, \\ \ln X_j^{ter} &= \ln X_j^{eut} + \ln a_j^{ter} - \ln a_j^{eut}, \\ X_k^{ter} &= 1 - X_k^{ter} - X_k^{ter}. \end{aligned} \tag{9}$$

Using the ratio (8):

$$\Delta H_i^{fus}/R(1/T_i^{fus} - 1/T) = \ln a_i,$$

we immediately obtain a system of equations for calculating the monovariant branch of crystallization of components $(i-j)$:

$$\begin{aligned} \ln X_i^{ter} &= \ln X_i^{eut} + \Delta H_i^{fus}/R(1/T_{ij}^{eut} - 1/T), \\ \ln X_j^{ter} &= \ln X_j^{eut} + \Delta H_j^{fus}/R(1/T_i j^{eut} - 1/T). \end{aligned} \tag{10}$$

The system of equations(10) has a number of obvious advantages over the geometric method, in particular:

1. Does not require any model description of binary subsystems;
2. More importantly, it does not require extrapolation of the crystallization branches of the components to sub-eutectic temperatures;
3. Allows calculating all coordinates of the triple eutectic (corresponding to crystallization $i - j - k$):

$$(T_{ijk}^{eut};\ X_i^{ter-eut},\ X_j^{ter-eut},\ X_k^{ter-eut} = 1 - X_i^{ter-eut} - X_j^{ter-eut}).$$

4. The system (10) allows checking with what accuracy it is quasi-simple, i.e., how rectilinear are the isotherms–isobars–isopotentials in it?

4. Thermodynamic algorithm for calculating diagrams of quasi-simple systems

To construct a melting diagram of a ternary system $i-j-k$, it suffices to solve 3 pairs of systems of equations of type (10) for 3 branches of joint crystallization of pairs of components

$(i-j)$:

$$\ln X_i^{ter} = \ln X_i^{eut} + \Delta H_i^{fus}/R(1/T_{ij}^{eut} - 1/T), \qquad (11.1)$$

$$\ln X_j^{ter} = \ln X_j^{eut} + \Delta H_j^{fus}/R(1/T_{ij}^{eut} - 1/T), \qquad (11.2)$$

$(i-k)$:

$$\ln X_i^{ter} = \ln X_i^{eut} + \Delta H_i^{fus}/R(1/T_{ik}^{eut} - 1/T), \qquad (11.3)$$

$$\ln X_k^{ter} = \ln X_k^{eut} + \Delta H_k^{fus}/R(1/T_{ik}^{eut} - 1/T), \qquad (11.4)$$

$(j-k)$:

$$\ln X_j^{ter} = \ln X_j^{eut} + \Delta H_j^{fus}/R(1/T_{jk}^{eut} - 1/T), \qquad (11.5)$$

$$\ln X_k^{ter} = \ln X_k^{eut} + \Delta H_k^{fus}/R(1/T_{jk}^{eut} - 1/T). \qquad (11.6)$$

A thermodynamic calculation of the melting diagram of the Na_2CO_3–NaF–NaCl system is shown below in Figure 1.

As can be seen from Figure 1, the thermodynamic calculation data is in convincing agreement with the available experimental data. The thermodynamic method does not require a large number of experimental data on the melting diagrams of binary subsystems for more or less accurate extrapolation (it requires only the coordinates of binary eutectic). The only sufficiently strict condition for the applicability of the thermodynamic calculation method is the requirement of „quasi-simplicity“, i. e. straightness of the liquidus isotherms.

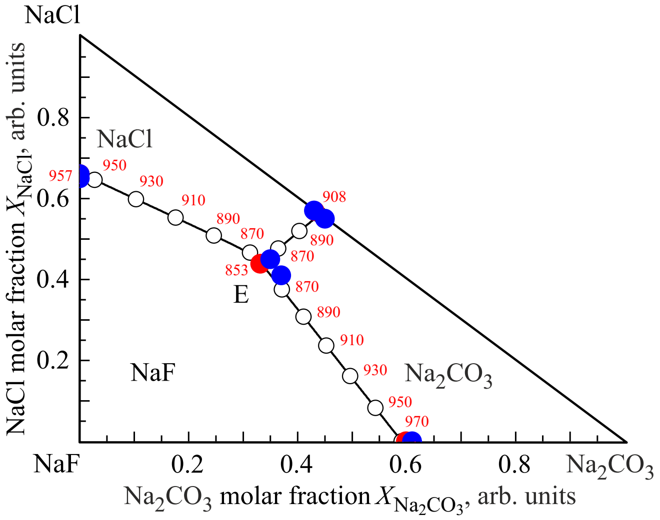

Figure 1. Melting diagram of the triple system Na_2CO_3–NaF–NaCl (lines and hollow circles — thermodynamic calculation, red circles — calculated eutectic, blue circles experimental data [13–15]), E — triple eutectic, the red numbers represent the liquidus temperatures.

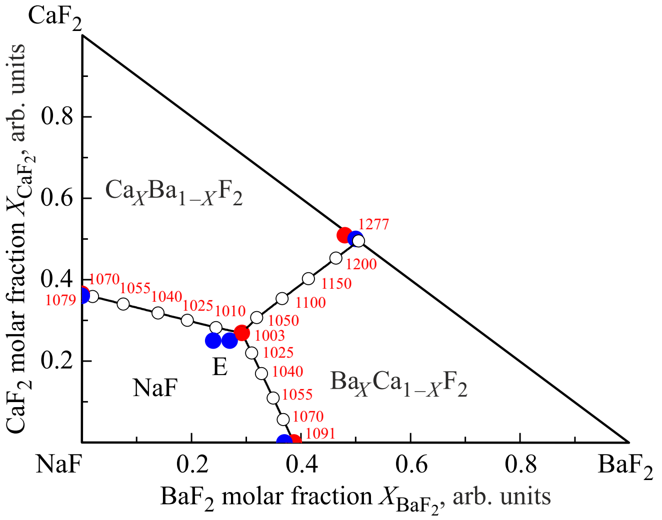

Figure 2. Melting diagram of the triple system NaF–BaF_2–CaF_2(lines and hollow circles — thermodynamic calculation, red circles — calculated eutectic, blue circles experimental data [13,18]), E — triple eutectic, the red numbers represent the liquidus temperatures.

If we consider all the melting diagrams of multicomponent systems of various physical nature and components ($n \geq 3$) available in the literature (including mutual ones with solid solutions, binary and ternary compounds, etc.) — see, for example, reference books [14–17], then the share of quasi-simple systems, according to our estimates, is 3–5 %.

To demonstrate the possibility of a thermodynamic calculation method using the example of the melting diagram of a quasi-simple ternary system NaF–BaF_2–CaF_2 with a common anion, the calculation results and experimental data are shown in Figure 2 [13,18].

The results of the thermodynamic calculation are in good agreement with experimental data, despite the fact that one of the binary subsystems BaF_2–CaF_2 implements a number of eutectic cubic solid solutions with a wide range of immiscibility: $Ca_XBa_{1-X}F_2$.

This algorithm is applicable to the thermodynamic calculation of any phase diagrams: melting diagrams, solubility diagrams, and phase equilibrium diagrams of liquid–vapor, including systems containing water-soluble nanoclusters. As an example, Figure 3 shows a diagram of solubility in a ternary system containing 2 water-soluble light fullerene adducts C_{60} with amino acids:

$$C_{60}(C_6H_{15}N_2O_2)_2 - C_{60}(C_4H_8NO_3)_2 - H_2O \text{ by } 298\,K.$$

Figure 3 shows a good agreement between the calculation results and the experiment.

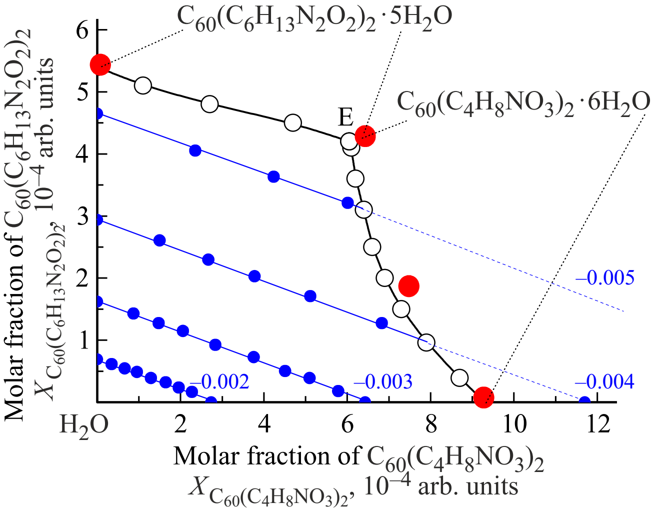

Figure 3. Diagram of solubility in the ternary system $C_{60}(C_6H_{15}N_2O_2)_2$–$C_{60}(C_4H_8NO_3)_2$–$H_2O$ at 298 K: black circles and lines — calculation of the solubility diagram, red circles experimental data of the authors, blue lines and dots — isopotentials of water, blue dotted line — they are also in the metastable supersaturated region, the values of the logarithm of water activity ($\ln a_W$) are represented by blue numbers, E — triple eutonics.

5. Conclusion

The paper presents a non-model algorithm for calculating melting diagrams of multicomponent quasi-simple systems (with rectilinear liquidus isotherms in the crystallization fields of components) from data on melting diagrams of binary subsystems that make up them. The application of the algorithm is demonstrated by the example of melting diagrams of triple quasi-simple salt systems with a common cation and a common anion.

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Conflict of interest

The authors declare that they have no conflict of interest.

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