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Research Article

Non-model Calculation of Fusibility Diagrams of Quasi-simple Systems on the example of Electrolyte and Non-electrolyte Systems

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Abstract

The article presents a non-model algorithm for calculating the fusibility diagrams of multicomponent systems exclusively from data on the fusibility diagrams of binary subsystems. The first geometric calculation algorithm is based on solving systems of linear equations of liquidus isotherms. The second, thermodynamic calculation algorithm requires only the coordinates of the binary eutectic. The application of both algorithms is demonstrated by the example of fusibility diagrams of ternary quasi-simple salt systems with a common cation and a common anion. There is a convincing agreement between the calculation results the results of the non-model calculation with the available experimental literature data. The proof of the fact that all non-invariant points of various quasi-simple ternary systems (with two identical and one different component) belong to one mono-variant curve is given. Examples of calculations of these mono-variant curves are given and convincing agreement of the non-model calculation with experimental data is demonstrated. A system of transcendental equations has been compiled for calculating the coordinates of ternary eutectic.

1. Introduction

Let us introduce the basic definitions and concepts used in this work:

- Fusibility or melting diagram – is one of the main types of phase equilibrium diagrams, establishing the relationship between the composition of the equilibrium melt and the equilibrium solid phases, with the remains of the equilibrium phases connected by nodes - straight line segments or sometimes omitted;
- Quasi-simple systems are the systems with straight-line isopotentials of components (lines with the constant chemical potentials of components);
- Pseudo-ideal system is special case of systems for fusibility diagrams with straight liquidation isotherms in the crystallization fields of solid phases of constant composition);
- Liquidus isotherms - figurative points of melt compositions with the same temperature of the appearance of the first crystals during cooling of the system;

- Non model calculation is calculation without using any empirical or semi-empirical thermodynamic models6 for example: regular, quasi- or subregular melts, ideally associated melts, EFLCP, NRTL etc.

- Mono-variant curve is in fusibility diagrams, a line of equilibrium between melts and solid phases along which movement is possible without changing the number or nature of the equilibrium phases. The variance or number of degrees of freedom on such lines is equal to 1.

- Non-variant point is in fusibility diagrams, a point of equilibrium between melts and several solid phases along which movement is impossible without changing the number or nature of the equilibrium phases. The variance or number of degrees of freedom in such is equal to 0.

1.1. Properties of quasi-simple systems and related works

Let's introduce the basic definitions. A three- or more-component system ($n \geq 3$) will be called quasi-simple if the isotherms-isobars–is opotentials of a component of the system are straight line segments ($n = 3$), sectors of planes ($n = 4$) or hyperplanes ($n \geq 5$) (the isopotentials of the *i*-th component are the geometric location of figurative points of compositions with a constant value of the chemical potential $\mu_i = (\partial G / \partial n_i)_{T,P,n_{j\neq i}}$. It is important to note that the isopotentials of other salt components may or may not be linear - they represent straight segments or sectors of hyper-planes. 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 used dual terminology:

1.1.1. When describing isothermal-isobaric solubility diagrams, systems with linear 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 in ternary system:

$$\left.\frac{m_1}{m_1^0}\right|_{\mu_w} + \left.\frac{m_2}{m_2^0}\right|_{\mu_w} = 1 \quad (1)$$

where m_i and m_i^0 are the molalities of the *i*-th component in the ternary and binary solution with equal values of water chemical potential - μ_w or water activity - a_w, correspondingly $(\mu_w = \mu_W^{(0)}(T,P) + RTlna_w)$. In the case of *n*-component system the equation of isoactive hyperplane has the form:

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

1.1.2. When describing polythermal-isobaric fusibility diagrams of a system with linear liquidus isotherms (the latter are the geometric location of the figurative points of compositions with a constant value $T(^i)$ – the 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 also the isotherm-isobar-isopotentials of the *i*-th component of the system. According to the terminology of A.Storonkin's school [9-12], such systems are commonly called “pseudo-ideal". Thus, when considering the liquidus isotherms in the field of crystallization of an individual component, both concepts A) and B) are identical. In this case (since all components of the melt are equal), isotherms-isobars-isopotentials in the fields of other *j, k ≠ i* individual components of the system, as a rule, are also rectilinear.

Mathematically, the latter means in ternary system:

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

where x_1 and x^0_i are the molar fractions of the *i*-th component in the ternary and binary solution with equal values of liquidus temperature - $T^{(l)}$. In the case of *n*-component system the equation of isolative hyperplanes has the form:

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

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 So, because it's fair:

$$m_i = (n_i / n_w)\cdot 55.1\ (i \neq W),\ X_i = (n_i / \sum_{j=1}^{n} n_j), 55.51 \sim 1000/18 \quad (5)$$

then equations (1) - (4) can be transformed to the form:

$$\sum_{i=1}^{n} \alpha_i n_i + \alpha_0 = 0 \text{ or } L(n_i) = 0 \quad (6)$$

where: a_i are coefficients of the linear form *L.*

In the future, following the authors of [7,8], we will combine both classes of systems considered here with the general term "quasi-simple systems".

2.1. Phase diagrams of solubility and liquid-vapor quasi-simple systems and related works

Earlier in [7], a non-model thermodynamic algorithm was developed for calculating thermodynamic functions (chemical potentials and activities of components – μ_i and a_i) for given values of state parameters (temperature, total pressure, and chemical potential of solvent - water - *T, P,* μ_W) and constructing solubility diagrams of quasi-simple systems based solely on binary data subsystems *i-W* - $a_W(m_i)$. In particular, for the simplest case of solubility diagrams of three-component systems with crystallization of solvate (anhydrous) components on the crystallization branch of the 1st component, the following relations are valid (1, 2 are the numbers of dissolved components, 3 is the *W* number of the solvent):

$$lnm_i^{ter} = lnm_i^{sups-bin} + lna_i^{sat-bin} - lna_i^{sups-bin} \quad (7)$$

$$lnZ_i = lna_i^{sat-bin} - lna_i^{sups-bin} < 0 \quad (8)$$

$$lnm_j^{ter} = lnm_j^{sups-bin} + lnZ_j \quad (9)$$

where, for a given solvent activity (a_w = *const)* : $m_i^{sups-bin}(a_W)$ is the concentration of a metastable supersaturated solution in the binary subsystem *i – W;* $a_i^{sups-bin}(a_W)$ is the activity of *i*–th component in metastable supersaturated solution in the binary subsystem *i – W;* $a_i^{sat-bin}$ is the activity in stable saturated solution in the binary subsystem *i – W;* $lna_i^{sat-bin} = lnSP_i$ is the thermodynamic potential of the *i*–th solid phase (independent of the value a_w); Z_i is the Yankee index of the *i*–th component of the solution or the mole fraction in the solvate–free concentration space [7]. The only visible disadvantage of the proposed algorithm is the need to extrapolate the dependence of solvent activity on the concentration of binary solutions to supersaturated solutions. An example of calculating the solubility diagram of the *NaCl – KCl – H_2O* system at 25°C is shown in Figure 1 in the Supplement to the article. There are also numerous generalized experimental data from the solubility guide [13], which are in excellent agreement with the results of non-model calculations for binary systems. In article [7], algorithms for calculating solubility diagrams of systems with crystallization of electrolytes of different valence types, crystallization of crystal-hydrates, ternary compounds of constant composition, and solubility diagrams of quadruple systems are demonstrated. The calculation also turns out to be very accurate.

Earlier in [8], a non-model thermodynamic algorithm was developed for calculating thermodynamic functions (chemical potentials, activities, and partial pressures of volatile components – μ_i, a_i, P_i) for given values of state parameters (temperature, total pressure, and chemical potential of solvent -water – *T, P,* μ_W) and constructing diagrams of liquid-water equilibria.pairs of quasi-simple systems, exclusively from data on binary subsystems *i -W* - $a_w(m_i)$ The equations for calculating the activity of the *i*-th volatile component of the ternary solution - a_i^{ter} and P_i^{ter} have the following form:

$$\ln a_i^{ter} = \ln a_i^{bin} + \ln Z_i \quad (10)$$

$$\ln P_i = \ln a_i^{ter} + \ln K_{H,i}^m \quad (\text{at } a_w = \text{const}) \quad (11)$$

Where at the given water activity (a_w = *const);* $a_i^{bin}(a_W)$ – activity of *i*–th component in binary system *i–W;* a_i^{ter} – activity of *i*–th component in ternary system, Z_i is the Yeneke index of the *i*–th component of the solution or the mole fraction in the solvate–free concentration space (see equation (8)), P_i – partial pressure of *i*–th volatile component in ternary system , $K_{H,i}^m$ – Henry constant of *i*–th volatile component, determined in binary subsystem *i-W.* Solvent partial pressure P_w, determined by Raul's law [14]:

$$\ln P_i = \ln a_w + \ln P_w^0 \quad (12)$$

where: P_w^0 - the vapor pressure above the pure solvent under the conditions under consideration (tabulated, for example, for H_2O at 25°C, at P 1 atm. = 23.76 mm Hg). Sum vapor pressure, P_{sum}, according to Dalton law:

$$\ln P_{sum} = \sum_{i=vc} a_i^{(i-w)} Z_i K_{H,i}^m + a_w P_w^0 \quad (13)$$

Where, the summation is carried out for all volatile components and volatile solvent. An example of calculating the solubility diagram of the *KCl – HCl – H_2O* system at 25°C is shown in Figure 2 in Supplement to the article. There are also quite rare direct experimental data on the partial pressures of volatile components from [15], which are in perfect agreement with the results of non-model calculations for binary systems. Algorithms for calculating solubility diagrams of systems with one, two, and three volatile components in ternary and quaternary quasi-simple systems are also demonstrated in [8].

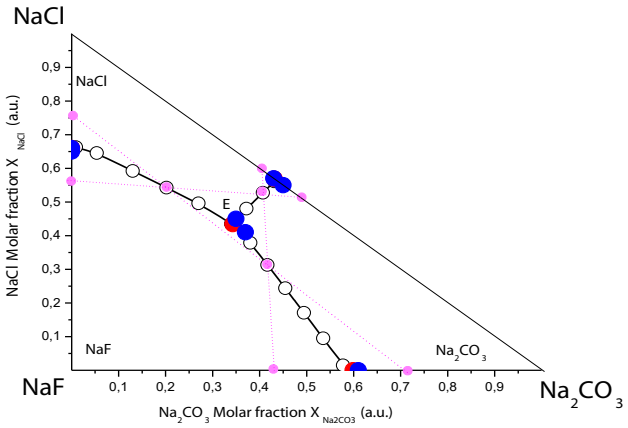

Figure 1: Fusibility diagram in ternary systems Na_2C0_3 – *NaF* - *NaCl* (lines and hollow circles are geometrical calculations, red circles are calculated eutectics, blue circles are experimental data [28, 46, 47]). Purple dotted lines and circles demonstrate an algorithm for constructing mono-variant curves by intersecting straight isotherms of the liquidus (in the example in Figure 1, corresponding to a temperature of 910 K), E – ternary eutectic.

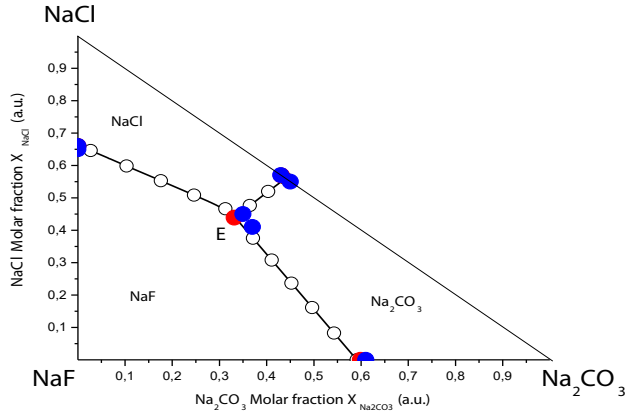

Figure 2: Fusibility diagram of the Na_2C0_3 – *NaF* - *NaCl* ternary system (lines and hollow circles are thermodynamic calculations, red circles are calculated eutectic, blue circles are experimental data [28, 46, 47]), E is ternary eutectic.

The main goal of this article is to transfer the previously developed algorithm for calculating phase diagrams of multicomponent quasi-simple systems exclusively from data on binary subsystems of their components.

2. Thermodynamic substantiation of the algorithm for calculating the melting diagrams of quasi-simple systems

2.1. Consequence of fundamental thermodynamic equations

Intuitively, it is quite clear that in the case of quasi-simple ternary or more component systems, the thermodynamic properties must inevitably be completely determined by the properties of the binary subsystems that make up them. This fact follows directly from the need to fulfill the fundamental Gibbs–Duhem equation and the cross-differentiation conditions for the liquid phase of an n-component system under isothermal-isobaric conditions [9,10,16]:

$$\sum_{i=1}^{n} n_i \sum_{j=1}^{n} (\partial \mu_i / \partial n_j) dn_j = 0 \quad (14)$$

$$\partial \mu_i / \partial n_j = \partial \mu_j / \partial n_i \quad (15)$$

Where: n_i – the number of moles of the *i*-th component of the liquid phase of variable composition. In the case where the composition of the system belongs to the isopotential of a component (a solvent for solubility diagrams or one of the eqivalent components of the melt for fusibility diagrams, we assign the number *n* to this component), the equation is added to the system of differential equations (14), (15):

$$\sum_{i=1}^{n} (\partial \mu_n / \partial n_i) dn_i = 0 \quad (16)$$

And in the case of quasi-simple systems, an equation belonging to a linear form of type (6) is added to these equations:

$$\sum_{i=1}^{n} \alpha_i dn_i = 0 \text{ or } L(dn_i) = 0 \quad (17)$$

Thus, excess thermodynamic functions in multicomponent liquid phases (component activities - a_i, their chemical potentials - $_i$), as well as diagrams of liquid-vapor phase equilibria *(l-v),* solubility and fusibility *(s-l)* diagrams of multicomponent systems should be calculated directly from data on thermodynamic functions of binary subsystems. Indeed, for example, for a three-component liquid phase n = 3, to describe the thermodynamic properties of the latter at *T, P = const*, it is sufficient to determine the functional dependence of the Gibbs potential G (n_1, n_2, n_3)*

To do this, it is enough to determine the values of 9 partial derivatives - $(\partial\mu_i / \partial n_j)$, of which, only 3 are independent under the conditions under consideration (3 are excluded by conditions (15), and 3 more by belonging to a linear form *L* (17): $dn_i / dn_j = -\alpha_j / \alpha_i$). The remaining 3 equations to determine $(\partial\mu_i / \partial n_j)$ - these are equations (14), (16) and an additional equation limiting the number of moles of the system components: $\sum_{i=1}^{n} n_i = 1; \sum_{i=1}^{n} dn_i = 0$ when using the molar fraction scale in melts, or: $n_n = n_W = \frac{1000}{M_W}; dn_W = 0$ when using the molality scale in solutions. Belonging to a specific liquidus temperature in the melting diagram of a specific solvent iso-potential line in the solubility diagram is determined by the value of the free term in linear form *L* - α_0 (6) or the integration constant in differential form (17).

2.2. Topological isomorphism of phase diagrams and related works

The fact of the complete iso-structure of the Van-der-Waals differential equations is well known, describing diagrams of liquid-vapor phase equilibria (at constant temperature or pressure), fusibility diagrams (at constant pressure) and solubility diagrams (at constant temperature and pressure simultaneously) [4,17,18]. At the same time, the number of components in the solubility diagrams is 1 more, than in other diagrams to describe the solubility diagrams. To describe solubility diagrams, the metric of the Korzhinsky potential (or incomplete Gibbs potential, abbreviated for solvent) is used, which is characteristic in variables such as temperature, pressure, the number of moles of dissolved components, and the chemical potential of the solvent [4,19,20].

Other phase diagrams are described in the metric of the usual Gibbs potential, which is characteristic in variables such as temperature, pressure, and the number of moles of all system components. The consequence of the iso-structure of differential equations is a complete topological isomorphism of phase diagrams of various types, in particular, diagrams of solubility of *(n+1)*-component systems in variables: $\mu_W - \vec{Z}$ and fusibility diagrams in the variables: $T - \vec{X}$ (where: $\vec{Z}$ – the vector of the solution composition in the reduced solvent-free concentration space of the Yenecke indixes, $\vec{X}$ - the vector of the melt composition in the total concentration space of molar fractions). Thus, if the authors of [7,8] succeeded in developing a universal algorithm for calculating solubility diagrams and diagrams of liquid-vapor phase equilibria of quasi-simple systems, then the authors of this work have the right to assume that an analog of this algorithm exists for melting diagrams of quasi-simple systems.

2.3. Algorithms and methodology of model calculations

Another reason for searching for a thermodynamic method and algorithm for calculating the melting diagrams of quasi-simple systems is the fact that there are a number of model algorithms for calculating the phase diagrams of such systems. Here are just 2 examples.

V. Filippov and co-authors proposed a method for calculating solubility diagrams of ternary systems using K. Pitzer's equations [21,22] from data on binary subsystems [23,24]. Binary Pitzer parameters [21] are used to determine the compositions of binary solutions corresponding to different values of solvent activity $m_i^{(bin)}(a_w), i = 1,2)$. Then an artificial array is constructed from calculated rectilinear solvent isoactivates in a ternary system $a_w^{ter}(m_1, m_2)$ and the ternary parameters of the Pitzer equations are found [23]. Then, using the binary and ternary Pitzer parameters and the values of the thermodynamic potentials of the solid phases (determined by solubility in binary subsystems), the authors performed a trivial calculation of the solubility diagram of the ternary system. At the same time, the straightness of the isoactivated solvent does not mean that the ternary Pitzer parameters are equal to zero [4,23,24].

A similar example of model calculation of fusibility diagrams of ternary quasi-simple systems using the semi-empirical EFLCP model [25-27] is also associated with the following set of operations: model description of fusibility diagrams of binary subsystems and finding binary parameters of EFLCP; finding compositions of binary systems (corresponding to certain liquidus temperatures); construction of an artificial array T(X_1,X_2) and finding ternary parameters EFLCP; construction of fusibility diagram of ternary system.

The authors again believe that if it is possible to calculate diagrams of phase equilibria of multicomponent systems, using thermodynamically consistent semi-empirical models, then there may be a non-model method of such calculation.

2.4. Geometric method for calculating diagrams of quasi-simple systems

This calculation method is quite understandable. For such a calculation, it is sufficient to carry out the most accurate description of the fusibility diagrams of the binary subsystems of the multicomponent system under consideration, and in the temperature range corresponding to metastable super-cooled melts. Such a description can be carried out in various ways: from accurate direct experimental data (which is relatively rare), within the framework of any consistent thermodynamic model, or even using a simple mathematical model capable of extrapolation, for example, B-Spline. The only and main difference from the approaches described above in the section "Algorithms of model calculations" is the fact that we use algorithms or models for describing ternary systems, i.e. the use of moles is strictly limited to binary subsystems. For an example of calculation, consider a ternary salt system with a common cation.

2.5. System Na_2CO_3(1) – NaF (2) – NaCl(3)

This system is interesting because both for itself and for all its binary subsystems there are reliable and well-consistent experimental data on fusibility diagrams [28-45], and the system itself is quasi-simple with a very high probability and accuracy. To describe the fusibility diagrams of all three binary subsystems, we used a simple iso-osmotic model. The crystallization branch of the *i*-th component of the *i-j* system is valid:

$$\Delta H_i^{fus} / R(1/T_i^{fus} - 1/T) = lna_i = \tilde{\varphi}_{ij} lnX_i \quad (18)$$

where: ΔH_i^{fus} - molar enthalpy of fusion of *i*-th component, T_i^{fus} – temperature of fusion, a_i, X_i – activity and molar fraction of *i*-th component in saturated melt, $\tilde{\varphi}_{ij}$ – osmotic coefficient in the system *i-j*, independent on temperature and composition, $\tilde{\varphi}_{ij} = \tilde{\varphi}_{ji}$.

$$\Delta H_i^{fus} = \Delta H_i^{fus}\left(T_i^{fus}\right) + \int_{T_i^{fus}}^{T} \Delta C_{P,i}(T)\,dT \approx \Delta H_i^{fus}\left(T_i^{fus}\right) + \overline{\Delta C}_{p,i}(T - T_i^{fus})$$

$$\Delta C_{P,i}(T) = C_{P,i}^{l}(T) - C_{P,i}^{s}(T) \approx \overline{\Delta C}_{P,i} = \overline{C_{P,i}^{l}} - \overline{C_{P,i}^{s}} \quad (19)$$

where: $C_{P,i}^{l}(T), C_{P,i}^{s}(T)$ – temperature functions of the molar isobaric heat capacity of the *i*-th component in the melt and solid phase, respectively, $\overline{C_{P,i}^{l}}, \overline{C_{P,i}^{s}}$ – it's average values at $T = T_i^{fus}$.

Data on the properties of individual components, unified osmotic coefficients, and coordinates of binary eutectic are presented in Tables 1, 2, and Figure 3 of the Supplement. It is clearly seen from Figure 3 that the simplest isosmotic model is quite sufficient for an accurate description of the melting diagrams of binary subsystems.

Numerical calculated data on the melting diagrams of binary subsystems, including supercooled melts, are presented in Table 3 Applications. Let's take a closer look at the algorithm for calculating the melting diagram of a ternary system using the geometric method. Fix the temperature of the liquidus – *T*. The equations of the direct isotherms of the liquidus in the crystallization fields of different *i*-th solid phases (they are also iso-activates of the *i*-th components), written in segments, have the form:

NaCl – iso-activate: $X_1.1/(1 - X_{NaCl}^{02}) + X_2.1/(1 - X_{NaCl}^{01}) = 1$ (20.1)

NaF –iso-activate: $X_1.(X_{NaF}^{01} - X_{NaF}^{02})/X_{NaF}^{01}(1 - X_{NaF}^{02}) + X_2.1/X_{NaF}^{01} = 1$ (20.2)

Na_2CO_3–iso-activate: $X_1.1/X_{Na_2CO_3}^{01} + X_2.(X_{Na_2CO_3}^{01} - X_{Na_2CO_3}^{02})/X_{Na_2CO_3}^{01}(1 - X_{Na_2CO_3}^{02}) = 1$ (20.3)

where: X_1, X_2 – molar fractions of Na_2CO_3 *and NaF* in ternary melt;

X_{NaCl}^{01} – molar fraction of *NaCl* on the crystallization curve of *NaCl* in binary system *NaCl - NaF*; X_{NaCl}^{02} – molar fraction of *NaCl* on the crystallization curve of *NaCl* in binary system *NaCl* - Na_2CO_3; X_{NaF}^{01} – molar fraction of *NaF* on the crystallization curve of *NaF* in binary system *NaF - NaCl*; X_{NaF}^{02} – molar fraction of *NaF* on the crystallization curve of *NaF* in binary system *NaF* - Na_2CO_3; $X_{Na_2CO_3}^{01}$ – molar fraction of Na_2CO_3 on the crystallization curve of Na_2CO_3 in binary system Na_2CO_3 - *NaCl*; $X_{Na_2CO_3}^{02}$ – molar fraction of Na_2CO_3 on the crystallization curve of Na_2CO_3 in binary system Na_2CO_3 - *NaF* (Table 3).

To calculate the monovariant curves of the joint crystallization of two salts consisting of points representing the intersections of two of the three liquidus isotherms, it is necessary to solve systems of 2 of 3 different equations of the lines (20.1) – (20.3). As a result, we obtain:

The branch of joint crystallization of *NaCl+NaF* – equations (20.1) and (20.2):

$$\Delta_1 = 1/(1-X^{02}_{NaCl})\left(X^{01}_{NaF}\right) - (X^{01}_{NaF} - X^{02}_{NaF})/X^{01}_{NaF}(1-X^{02}_{NaF})(1-X^{01}_{NaCl});$$

$$\Delta_1^1 = 1/X^{01}_{NaF} - 1/(1-X^{01}_{NaCl});$$

$$\Delta_1^2 = 1/(1-X^{02}_{NaCl}) - (X^{01}_{NaF} - X^{02}_{NaF})/(1-X^{02}_{NaF})X^{01}_{NaF};$$

$$X_1 = \Delta_1^1/\Delta_1; X_2 = \Delta_1^2/\Delta_1 \quad (21.1)$$

The branch of joint crystallization of $NaF+Na_2CO_3$ – equations (20.2) and (20.3):

$$\Delta_2 = [(X^{01}_{NaF} - X^{02}_{NaF})/X^{01}_{NaF}(1-X^{02}_{NaF})]\,[(X^{01}_{Na_2CO_3} - X^{02}_{Na_2CO_3})/X^{01}_{Na_2CO_3}(1-X^{02}_{Na_2CO_3})] - 1/[X^{01}_{NaF}X^{01}_{Na_2CO_3}];$$

$$\Delta_2^1 = [(X^{01}_{Na_2CO_3} - X^{02}_{Na_2CO_3})/X^{01}_{Na_2CO_3}(1-X^{02}_{Na_2CO_3})] - 1/X^{01}_{NaF};$$

$$\Delta_2^2 = [(X^{01}_{NaF} - X^{02}_{NaF})/X^{01}_{NaF}(1-X^{02}_{NaF}) - 1/X^{01}_{Na_2CO_3};$$

$$X_1 = \Delta_2^1/\Delta_2; X_2 = \Delta_2^2/\Delta_2 \quad (21.2)$$

The branch of joint crystallization of $NaCl+Na_2CO_3$ – equations (20.2) and (20.3):

$$\Delta_3 = [1/(1-X^{02}_{NaCl})]\,[(X^{01}_{Na_2CO_3} - X^{02}_{Na_2CO_3})/X^{01}_{Na_2CO_3}(1-X^{02}_{Na_2CO_3})] - 1/[X^{01}_{Na_2CO_3}(1-X^{01}_{NaCl})];$$

$$\Delta_3^1 = [(X^{01}_{Na_2CO_3} - X^{02}_{Na_2CO_3})/[X^{01}_{Na_2CO_3}(1-X^{02}_{Na_2CO_3})] - 1/(1-X^{01}_{NaCl});$$

$$\Delta_3^2 = 1/(1-X^{02}_{NaCl}) - 1/X^{01}_{Na_2CO_3};$$

$$X_1 = \Delta_3^1/\Delta_3; X_2 = \Delta_3^2/\Delta_3 \quad (21.3)$$

The main calculation equations for geometrical method - equations (21.1) - (21.3) are related in trios. And all trios are independent. Each trio is responsible for calculating one monovariant curve (there are three in total), which must all intersect at one non-variant point. The results of calculating the melting diagram of the ternary system are presented in the Table 4 of Supplement and in article in Figure 1. The few experimental data available in the literature are also presented there for comparison. As can be seen from Figure 1 there is generally a fairly convincing agreement between the results of the geometric calculation and the experiment, which fully corresponds to the accuracy of the calculation in binary subsystems - Figure 3 in Supplement.

2.6. Substantiation of the basic formula of non-model calculation

The basic calculation formula is now justified by adapting the thermodynamic description of quasi-simple systems given in [7,8] to quasi-simple fusibility diagrams. So, let's consider an n-component melt of composition ($\vec{X}^{mult}$) formed by mixing n binary melts of composition (X_i^{bin}) taken at the same temperature *T*, and during this mixing the temperature of the ternary solution did not change. It was shown earlier in [7,8] that the change in the Gibbs potential during the formation of such 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):

$$G_{mix}/RT = \sum_{i=2}^{n} Z_i \ln Z_i = \sum_{i=2}^{n} Z_i \ln(\ln a_i^{mult} - \ln a_i^{bin}) \quad (22)$$

where: a_i^{mult}, a_i^{bin} – activity of *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 in the solubility diagrams [7,8] and we retain the designation:

$$Z_i = \frac{X_i^{mult}}{X_i^{bin}}, \sum_{i=1}^{n} Z_i = 1 \quad (23)$$

From (23) it follows, that:

$$\ln X_i^{mult} - \ln X_i^{bin} = \ln a_i^{mult} - \ln a_i^{bin} \quad (24)$$

which we will call the equation of quasi-simple systems. Let us now consider a ternary system (index *((ter = i-j-k))*, namely, a branch of the joint crystallization of components *(i-j)* starting from a binary non-invariant eutectic point with coordinates:

$T_{ij}^{eut}; X_i^{eut} = 1 - X_j^{eut}$). (Let us now apply the basic equation (24) to a ternary melt of composition X_i^{ter} at temperature T and a eutectic binary melt of composition X_i^{bin}:

$$lnX_i^{ter} - lnX_i^{bin} = lna_i^{ter} - lna_i^{ter}$$

$$lnX_i^{eut} - lnX_i^{bin} = lna_i^{eut} - lna_i^{ter} \quad (25)$$

Applying the reasoning to both components, we get:

$$lnX_i^{ter} = lnX_i^{eut} + lna_i^{ter} - lna_i^{eut}$$

$$lnX_j^{ter} = lnX_j^{eut} + lna_j^{ter} - lna_j^{eut}$$

$$X_k^{ter} = 1 - X_k^{ter} - X_k^{ter} \quad (26)$$

Using equation (18): $\Delta H_i^{fus} / R(1/T_i^{fus} - 1/T) = lna_i$, we immediately obtain a system of equations for calculating the mono-variant crystallization branch of the components *(i-j):*

$$\begin{aligned} lnX_i^{ter} &= lnX_i^{eut} + \Delta H_i^{fus} / R\left(1/T_{ij}^{eut} - 1/T\right) \\ lnX_j^{ter} &= lnX_j^{eut} + \Delta H_j^{fus} / R\left(1/T_{ij}^{eut} - 1/T\right) \end{aligned} \quad (27)$$

1. The system of equations (27) has a number of obvious advantages over the geometric method, in particular:It 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 you to directly (with a certain accuracy – see below) calculate all the coordinates of the trernary eutectic (corresponding to crystallization *i-j-k* components): $T_{ijk}^{eut}; X_i^{ter-eut}, X_j^{ter-eut}, X_k^{ter-eut} = 1 - X_i^{ter-eut} - X_j^{ter-eut}$).

4. As strange as it may seem at once, system (27) allows us to check with what accuracy the system is quasi-simple, i.e. how rectilinear are the isotherms-isobars-isopotentials in it?

2.7. Thermodynamic method for calculating diagrams of quasi-simple systems. Results and discussion

The difference between the geometric method for calculating of fusibility diagrams (calculating the intersections of straight lines of liquidus isotherms) and the thermodynamic method for the same calculation is the absence of such a calculation and the need to extrapolate liquidus isotherms to supercooled metastable melts (here, only data on the coordinates of binary eutectics of subsystems are used).

To construct a melting diagram of the ternary *i-j-k* system, it suffices to solve 3 pairs of systems of equations of type (27) for 3 branches of joint crystallization of pairs of components:

(i-j):

$$lnX_i^{ter} = lnX_i^{eut} + \Delta H_i^{fus} / R\left(1/T_{ij}^{eut} - 1/T\right) \quad (28.1)$$

$$lnX_j^{ter} = lnX_j^{eut} + \Delta H_j^{fus} / R\left(1/T_{ij}^{eut} - 1/T\right) \quad (28.2)$$

(i-k):

$$lnX_i^{ter} = lnX_i^{eut} + \Delta H_i^{fus} / R\left(1/T_{ik}^{eut} - 1/T\right) \quad (28.3)$$

$$lnX_k^{ter} = lnX_k^{eut} + \Delta H_k^{fus} / R\left(1/T_{ik}^{eut} - 1/T\right) \quad (28.4)$$

(j-k):

$$lnX_j^{ter} = lnX_j^{eut} + \Delta H_j^{fus} / R\left(1/T_{jk}^{eut} - 1/T\right) \quad (28.5)$$

$$lnX_k^{ter} = lnX_k^{eut} + \Delta H_k^{fus} / R\left(1/T_{jk}^{eut} - 1/T\right) \quad (28.6)$$

A variant of the thermodynamic calculation of the melting diagram of the previously considered Na_2CO_3 - *NaF* - *NaCl* system is shown below in Figure 2 and in the Table 5 of Supplement.

As can be seen from Figures 1, 2 and Tables 4, 5, the thermodynamic calculation data as a whole are in convincing agreement with both the available experimental data and the result of the thermodynamic calculation, which, in general, is not surprising. However, the thermodynamic method, firstly, is an order of magnitude less laborious and 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). To find the exact coordinates of the ternary eutectic

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

With 3 independent variables, it is necessary and sufficient to solve a system of three transcendental equations from the system (28.1)-(28.6) with respect to T_{ijk}^{eut} and 2 of the three eutectics molar fractions. There are 9 different solutions by the numbers of the selected equations (28.M)-(28.N)-(28.P): (M-N-P) = (1-2-3), (1-2-5), (2-3-5), (1-3-4), (1-3-6), (3-4-6), (2,4-6), (2-5-6), (4-5-6). Numerous calculations show, that, if the isotherms of the liquidus are really rectilinear and the coordinates of the binary eutectic are established accurately enough ($T_{ij}^{eut} \pm \delta T; X_i^{eut} \pm \delta X; \delta T \le 5$ K, $\delta X \le 0.02$ mol.fr.), then the coordinates of the ternary eutectic (the solution of 9 different variants of 3 of equations) are set with the same accuracy – see Table 5.

2.8. Restrictions on the use of the thermodynamic method

The only rather strict condition for the applicability of the thermodynamic calculation method is the requirement of "quasi-simplicity", i.e., the straightness of the liquidus isotherms. Very conditionally, we divide the considered ternary systems into formal classes:

2.8.1. If we consider ternary systems consisting of nonelectrolytes, for example, the fusibility diagrams of ternary oxide systems [48], the proportion of quasi-simple systems is, according to the authors, 3-5 rel. %.

2.8.2. If we consider ternary systems consisting of electrolytes, for example, the fusibility diagrams of ternary salt systems with a common cation or common anion [49], the share of such systems is estimated by the authors to be 5-7 rel. % for systems with a common cation and 2-4 rel. % for systems with a common anion.

2.8.3. In ternary inter-salt systems, the proportion of quasi-simple systems is quite small - 1-2 rel. % [49]. This is not surprising, since, unlike systems of classes 1 and 2, the liquidus isotherms in this case, in principle, cannot be absolutely linear even in simple eutectic systems. For example, at the Van Rijn points [4,12,17] (when the figurative points of the compositions of two solid phases and the melt in equilibrium with them are on the same straight line), the liquidus isotherms in the solid phase crystallization fields touch each other and the two-phase equilibrium is disrupted the curve. Thus, in at least 2 of the 4 solid phase crystallization regions, the liquidus isotherms cannot be absolutely linear. However, a number of ternary interaction systems still have a fairly simple set of liquidus isotherms in several crystallization regions at once.

2.8.4. If a mono-variant curve, involving a compound, is calculated, using a thermodynamic algorithm, then the absolute straightness of the liquidus isotherms in the crystallization fields is also incredible. Indeed, the latter should bend around the figurative junction point, forming closed curves (in the case of ternary junctions) or semi-closed curves cut off by the side of the concentration triangle (in the case of binary junctions).

2.8.5. If a number of solid solutions are formed in the system, the straightness of the liquidus isotherms is found in principle (although very infrequently ~ 2 rel.% [48,49]). However, in a system with a continuous series of solid solutions with points of extreme liquidus temperatures, straightness is also incredible, since the liquidus isotherms in this case either touch or bend around such figurative points.

2.8.6. Systems involving binary solid solutions with a wide miscibility gap may well be quasi-simple with rectilinear liquidus isotherms, similar to simple eutectic systems [48,49].

2.9. System $NaF – BaF_2 – CaF_2$

To demonstrate the possibilities of the thermodynamic calculation method using the example of the more rarely encountered fusibility diagram of a quasi-simple ternary system with a common anion in Figure 3, we present the calculation results in the $NaF – BaF_2 – CaF_2$ system. The data on the properties of the individual components of the system are presented in the Table 1 in Supplement, data on the compositions of binary eutectic substances are presented in the Table 6 in Supplement and also in Figure 3. Figure 3 also presents a few experimental data on the ternary system [28,58]. It is clearly seen that the thermodynamic calculation data are generally in convincing agreement with the available experimental data, despite the fact that one of the binary subsystems $BaF_2 – CaF_2$ implements a number of eutectic cubic solid solutions [56,57] with a wide range of immiscibility: $Ca_XBa_{1-X}F_2$. We estimated the regular non-ideality parameter within the framework of the *LDM* model [25]:

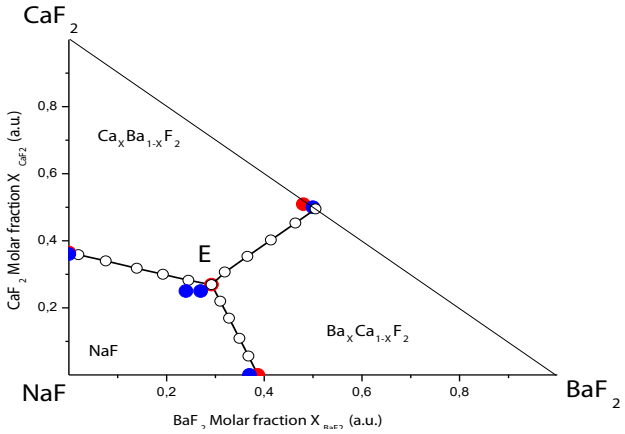

Figure 3: Fusibility diagram of the *NaF - BaF_2 – CaF_2* ternary system (lines and hollow circles are thermodynamic calculations, red circles are calculated eutectic, blue circles are experimental data [28, 50-58]), E is the ternary eutectic.

$$\alpha_{ij}^{(s)} = -8[\Delta H_{f,298}^{0}(i) + \Delta H_{f,298}^{0}(j)][(a(i) - a(j)) / (a(i) + a(j))]^2 \quad (29)$$

where: $\Delta H_{f,298}^{0}(i); \Delta H_{f,298}^{0}(j)$ standard heats of formation of compounds forming a solid solution (Given in the Supplement), *a(i), a(j)* – crystal lattice periods ($a(CaF_2)$ = 0.5451 *nm*; $a(BaF_2)$ = 0.6200 nm [60-62]). So, we obtained: $\alpha^{(S)}(CaF_2 - BaF_2)$ = *82.6 kj/mole*. Corresponding miscibility gap at the temperature of binary eutectic is: $X_{CaF_2}^{(s)}(1277\,K) = 0.07 \div 0.93\,mol.fr$; and at the temperature of ternary eutectic even wide: $X_{CaF_2}^{(s)}(1277\,K) = 0.05 \div 0.95\,mol.fr$. This circumstance practically does not affect the accuracy of the calculation by the proposed thermodynamic method.

3. A unified branch of the joint crystallization of two components in various quasi-simple systems. Methodology of calculation - Results and discussion

If we consider in detail the system of equations describing the construction of a mono-variant branch of the joint crystallization of two components *(i-j)* in a quasi-simple ternary system - (28.1), (28.2), then we can come to a rather paradoxical, at first glance, conclusion: All branches of the joint crystallization of the components *(i-j)* are fragments of the same mono-variant curve starting from the figurative point of the binary eutectic. On the other hand, this is expected, since the properties of a ternary system should be completely determined by the properties of binary subsystems. We will demonstrate a similar calculation of the *NaCl - NaF* joint crystallization curve in a set of 9 systems (of which 8 are ternary – see Figure 4). As can be seen from Figure 4, the *NaCl-NaF* crystallization lines for all quasi-simple *NaCl - NaF-X* ternary systemsms are indeed projected onto a single mono-variant curve with fairly high accuracy. At the same time, the temperatures of the eutectic correspond quite well to the calculated liquidus temperatures (including for 3 mutual systems). All these ternary non-variant points are represented also in summ

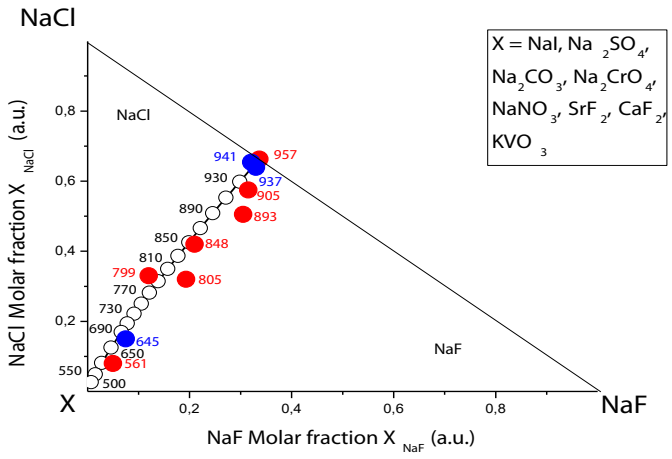

Figure 4: Calculated *NaCl-NaF* joint crystallization curve for 9 quasi-simple *NaCl-NaF-X* ternary systems (black lines and hollow circles are thermodynamic calculations, red circles are eutectic in ternary systems with a common cation, blue circles are eutectic in ternary reciprocal systems).

Table 1: Calculated *NaCl-NaF* joint crystallization curve and ternary eutectics for 9 quasi-simple *NaCl-NaF-X* ternary systems.

T(K)	X_{NaF} (mol.fr.)	X_{NaCl} (mol.fr.)	X_i (mol.fr.)	Solid phases	References
957	0,337	0.663	0.000	*NaF + NaCl*	from [30], P.742, 743
805	0.120	0.330	0.550	*NaF + NaCl + NaI*	[62]. From [49]. P.126.
893	0.305	0.505	0.190	$NaF + NaCl + Na_2SO_4$	[63]. From [49]. P.126-127.
905	0.212	0.375	0.375	$NaF + NaCl + NaF + Na_2SO_4$	[63]. From [49]. P.126-127.
848	0.210	0.420	0.370	$NaF + NaCl + Na_2CO_3$	[47]. From [49]. P.125.
799	0.193	0.320	0.487	$NaF + NaCl + Na_2CrO_4$	[64]. From [49]. P. 126
561	0.050	0.080	0.8670	$NaF + NaCl + NaNO_3$	[65]
937	0.330	0.639	0.031	$NaF + NaCl + SrF_2$ *from Na, Sr//Cl, Br*	[66]. From [49]. P.476.
941	0.321	0.654	0.0125	$NaF + NaCl + CaF_2$ *from Na, Sr//Cl, Br*	[67]. From [49]. P.247.
645	0.075	0.150	0.775	$NaF + NaCl + KVO_3$	[68]
957	0,33700	0,66300	0,00000	*NaF + NaCl + X*	Thermodynamic calculation
950	0,32672	0,64600	0,02729		
930	0,29826	0,59849	0,10325		
910	0,27120	0,55262	0,17618		
890	0,24554	0,50844	0,24603		
870	0,22129	0,46600	0,31271		
850	0,19846	0,42536	0,37618		
830	0,17706	0,38656	0,43638		
810	0,15708	0,34964	0,49328		
790	0,13851	0,31464	0,54685		
770	0,12134	0,28160	0,59706		
750	0,10555	0,25054	0,64390		
730	0,09112	0,22149	0,68739		
710	0,07801	0,19445	0,72754		
690	0,06619	0,16943	0,76439		
650	0,04622	0,12540	0,82838		
600	0,02759	0,08136	0,89105		
550	0,01499	0,04880	0,93621		
500	0,00721	0,02642	0,96637		

4. A method for verifying the compliance of ternary systems with the condition of quasi-simplicity - Straightness of liquidus isotherms

The a priori application of the thermodynamic calculation method is complicated by the obvious facts that:

4.1. There is clearly insufficient direct experimental data in the literature on the melting diagrams of ternary systems, although there is certainly a much larger set of such systems available to experiment compared to binary systems with the same components: $N_{ter} = C_n^3 = n(n-1)(n-2)/6 \gg N_{bin} = C_n^2 = n(n-1)/2$ (n – the number of available components of this class, for example, metal salts, oxides, sodium salts, fluorides ..., is usually in the tens, if not hundreds). Data on four or more component systems is even more relatively poor.

4.2. Often, even if data on monovariant and non-invariant equilibria are presented in the literature, data on liquidus isotherms in solid phase crystallization fields are absent or very scarce. There is practically no data on isothermal surfaces of the liquidus in four or more component systems.

4.3. Even if data on liquidus isotherms are available in ternary or more component systems, it is practically difficult to judge how reliable they are. For example, for data on fusibility diagrams at high temperatures (in which obtaining such data is the most laborious and least accurate), the liquidus isotherms are artificially straightened or constructed more or less arbitrarily based on data on binary subsystems.

4.4. In any case, it is often difficult, if not impossible, to reliably judge whether a multicomponent system is quasi-simple based on direct experimental data on binary subsystems. The question arises whether it is possible to judge how quasi-simple system is using only data on binary subsystems. Judging by the very formulation of the problem, such a method may exist.

Indeed, we will use the basic system of equations (28.1)-(28.6) and calculate the pairwise differences of equations (28.1) and (28.3); (28.2) and (28.5); (28.4) and (28.6). As a result, we obtain the following system of equations:

$$\Delta Q_i = Abs[\Delta H_i^{fus} / R\left(1/T_{ij}^{eut} - 1/T_{ik}^{eut}\right) - lnX_i^{eut}(i-k) + lnX_i^{eut}(i-j)] = 0 \quad (30.1)$$

$$\Delta Q_j = Abs[\Delta H_j^{fus} / R\left(1/T_{ij}^{eut} - 1/T_{jk}^{eut}\right) - lnX_i^{eut}(j-k) + lnX_i^{eut}(i-j)] = 0 \quad (30.2)$$

$$\Delta Q_k = Abs[\Delta H_k^{fus} / R\left(1/T_{ik}^{eut} - 1/T_{jk}^{eut}\right) - lnX_i^{eut}(j-k) + lnX_i^{eut}(i-k)] = 0 \quad (30.3)$$

where: T_{ij}^{eut} – temperature of binary eutectic in subsystem *(i - j)*; $X_i^{eut}(i-j)$ – molar fraction of *i*-th component in binary eutectic in subsystem *(i - j)*; ΔQ_i – modulus of deviation from the condition of quasi-simplicity (straightness of liquidus isotherms in a ternary system *(i – j - K)*, calculated from the *i*-th component. If the ternary system is ideally quasi-simple, and the coordinates of all binary eutect cs, as well as the functional dependences of the melting heats of all components, are absolutely accurate, then: $\Delta Q_i = \Delta Q_j = \Delta Q_k = 0$ Naturally, in reality this is unattainable. We will carry out the appropriate calculation for specific systems.

4.5.1. System *Na_2CO_3 – NaF – NaCl* : $\Delta Q_{NaF} \sim 0.07; \Delta Q_{NaCl} \sim 0.02; \Delta Q_{Na_2CO_3} \sim 0.07.$

Let's evaluate the result. To do this, we will perform an estimated calculation. Let's take the conditional temperature of the eutectic $T_{ij}^{eut} \sim 1000\,K$, typical error in its definition $\delta T_{ij}^{eut} \sim 20\,K$, typical heat of fusion $\Delta H_i^{fus} = 30\,kJ/mole$. Then, the expected error in the function definition is $\delta[\Delta H_i^{fus} / RT_{ij}^{eut}] \sim 0.07$. Corresponding error of the entire temperature part of the function ΔQ_j: $\delta[\Delta H_i^{fus} / R\left(1/T_{ij}^{eut} - 1/T_{ik}^{eut}\right)] \sim 0.10$. The value of the concentration of the *i*-th component in a binary eutectic with its participation is generally uncertain: $X_i^{eut}(i-k) = [0.0 \div 1.0]$. However, values $X_i^{eut}(i-k)$ close to 0.0 are nevertheless absolutely atypical, since eutectics belong to the very branch of crystallization of the *i*-th component. Let's take a fairly low value for certainty. $X_i^{eut}(i-k)$ (which gives the maximum error in the calculation): $X_i^{eut}(i-k) = 0.3\,mol.fr.$, and the expected error in its determination $\delta X_i^{eut}(i-k) = 0.02\,mol.fr.$ Then expected error in its determination $\delta[lnX_i^{eut}(i-k)] = 0.06$. The corresponding error of the entire concentration part of the function ΔQ_i: $\delta[-lnX_i^{eut}(i-k) + lnX_i^{eut}(i-j)] \sim 0.09$. In total, the expected error in defining the entire function is $\delta\Delta Q_i \sim 0.14$. Thus, it can be stated that the system under consideration is really quasi-simple, and the coordinates of the binary eutectic are quite accurate. In the following, we assume the condition that the ternary system is quasi-simple - functions for all components: $\Delta Q_i \leq 0.20$.

4.5.2. System *NaF – BaF_2 - CaF_2* : In this system with a common anion (which are less often and less accurately quasi-simple), the following values are obtained: $\Delta Q_{NaF} \sim 0.07; \Delta Q_{CaF_2} \sim 0.14; \Delta Q_{BaF_2} \sim 0.07.$ Thus, this system also seems to the authors to be really quasi-simple, although with noticeably lower accuracy compared to the previous one. The latter may be related to the formation of binary solid solutions in the system: $Ca_xBa_{1-x}F_2$ with a very wide miscibility gap.

4.5.3. System LiF – NaF - RbF: In conclusion, let us consider another ternary fluoride system, which is not quasi-simple. For it, the calculation based on experimental data on binary eutectic [69-73] gives the following values: $\Delta Q_{LiF} \sim 0.77; \Delta Q_{NaF} \sim 0.26; \Delta Q_{RbF} \sim 0.85.$ Thus, this system is in no way quasi-simple.

The quasi-simplicity criterion we present was obtained by examining several hundred systems of several classes (electrolyte and hydrocarbon non-electrolyte), and it is undoubtedly arbitrary. In the crystallization fields of compounds of constant composition, it cannot be applied in principle, since the liquidus isotherms in them are a priori nonlinear—they bend around the figurative junction point (at eutectic equilibria) or partially bend around it at peritectic equilibria. But even in such systems, quasi-simple parts of the systems can be encountered in the crystallization fields of individual components. If liquidus temperature extremes are realized in the diagrams of binary solid solutions, then the liquidus isotherms again cannot be linear, and the quasi-simplicity of such parts of the fusibility diagrams is impossible. This is because at such points, the liquidus isotherms touch the sides of the concentration triangle and cannot be linear.

5. Hydrocarbon systems

In conclusion, as an example, we present a similar calculation of the melting diagrams of quasi-simple ternary systems, based on hydrocarbons - alkanes (C_5-C_{10}) (Figure 5-9). As can be seen from Figures 5-9, these experimental data [74-76] are in quite convincing agreement with the calculations using the non-model algorithm for quasi-simple systems proposed by the authors. Data on the heats of fusion of hydrocarbons are taken from [81-93] and are presented in Table S7 of the Supplement.

Conclusion

The paper presents a non-model algorithm for calculating the fusibility diagrams of multicomponent quasi-simple systems (with linear liquidus isotherms in the crystallization fields of components) exclusively from data on the fusibility diagrams of

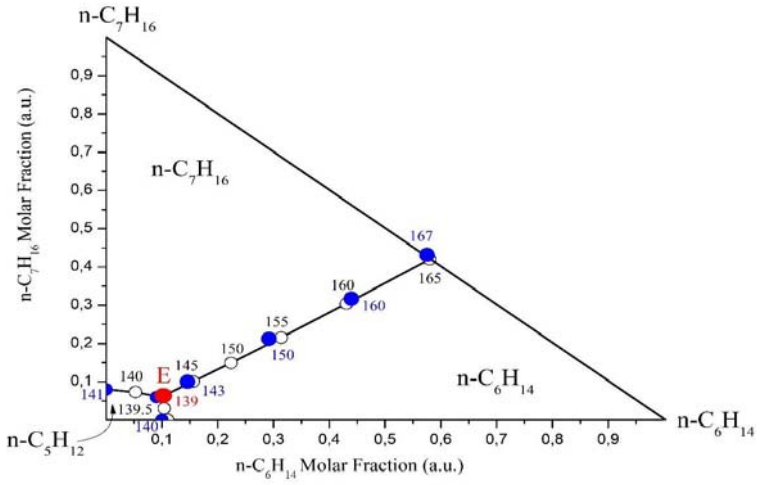

Figure 5: Fusibility diagram in ternary system n-C_5H_{12} - n-C_6H_{14} - n-C_7H_{16}: black lines and open circles – calculation; red point – eutectic nonvariant point (terminology – see [77-80]); blue circles - experimental data [74-76]; liquidus temperatures (K) are represented by figures.

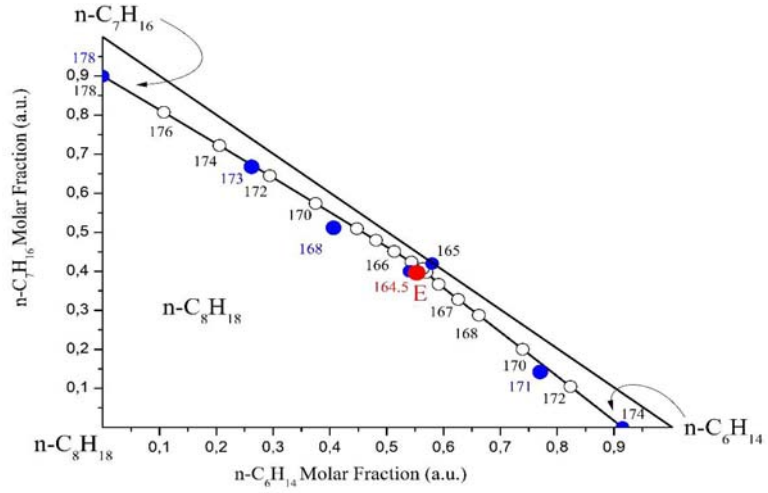

Figure 6: Fusibility diagram in ternary system n-C_8H_{18} - n-C_6H_{14} - n-C_7H_{16}: black lines and open circles – calculation; red point – eutectic nonvariant point (terminology – see [77-80]); blue circles - experimental data [74-76]; liquidus temperatures (K) are represented by figures.

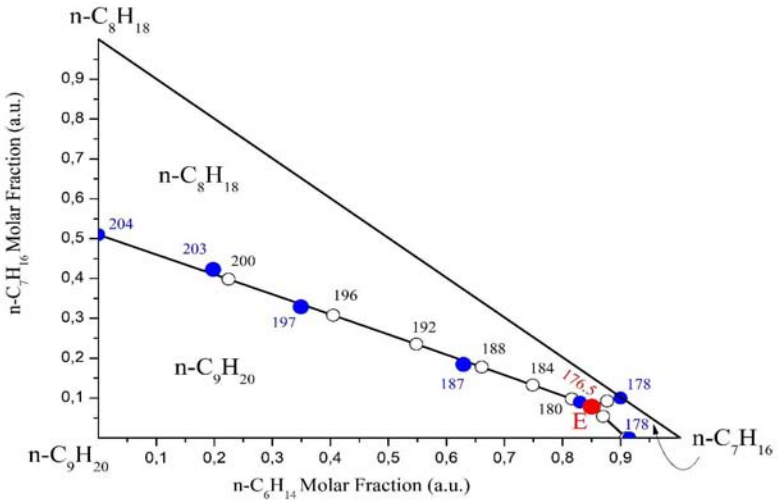

Figure 7: Fusibility diagram in ternary system n-C_9H_{20} - n-C_8H_{18} - n-C_7H_{16}: black lines and open circles – calculation; red point – eutectic nonvariant point (terminology – see [77-80]); blue circles - experimental data [74-76]; liquidus temperatures (K) are represented by figures.

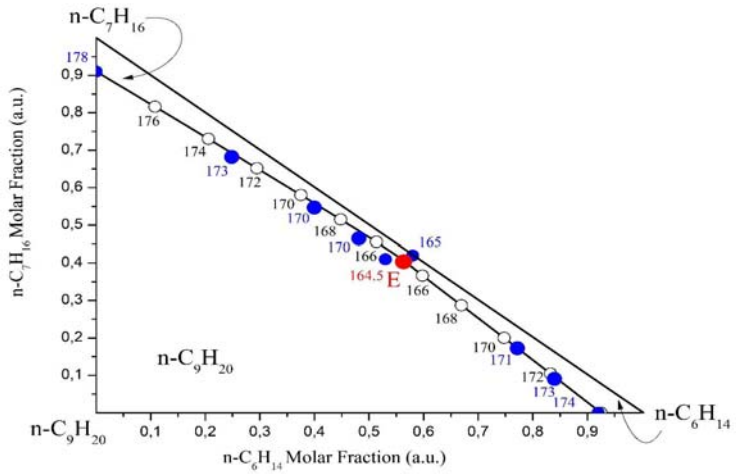

Figure 8: Fusibility diagram in ternary system n-C_9H_{20} - n-C_6H_{14} - n-C_7H_{16}: black lines and open circles – calculation; red point – eutectic nonvariant point (terminology – see [77-80]); blue circles - experimental data [74-76]; liquidus temperatures (K) are represented by figures.

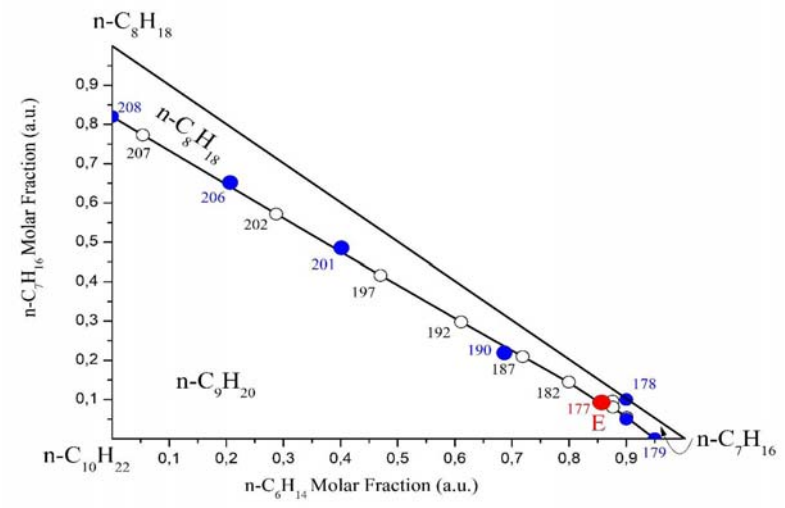

Figure 9: Fusibility diagram in ternary system *n-$C_{10}H_{22}$ - n-C_8H_{18} - n-C_7H_{16}*: black lines and open circles – calculation; red point – eutectic nonvariant point (terminology – see [77-80]); blue circles - experimental data [74-76]; liquidus temperatures (K) are represented by figures.

binary subsystems, which make up these systems. The application of the algorithm is demonstrated by the example of fusibility diagrams of ternary quasi-simple salt systems with a common cation and a common anion. On the other hand, there is a convincing agreement between the calculation results and the available experimental data in the literature. The proof of the fact that all non-variant points of various quasi-simple ternary systems (with two identical and one different component) belong to one mono-variant curve is given. A system of transcendental equations has been compiled for calculating the coordinates of ternary eutectic systems from data on binary eutectic systems of quasi-simple subsystems. A thermodynamic method for determining whether a multicomponent system belongs to the class of quasi-simple systems is proposed.

Authors acknowledge that the primary focus on calculating complex phase diagrams of multicomponent systems currently relies almost exclusively on model-based (usually semi-empirical) calculation methods, and recently even on artificial intelligence. Articles in the highly respected journal CALPHAD brilliantly confirm this. After reviewing issues from the past five years, we simply couldn't find even a statement about calculating phase diagrams based on first principles of thermodynamics: the principles of thermodynamics, conditions of phase and chemical equilibrium, stability criteria, etc. Our method, however, exclusively utilizes such non-model assumptions and therefore seems to the authors worthy of at least some attention.

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Contribution of the authors

N.A.C., V.A.K, M.V.K. - conceptualization, development of thermodynamic algorithm; N.A.K., M.S., D.V.K. – development of geometrical algorithm of calculation; B.N.A., D.S.D, - selection and verification of experimental data; M.V.C, M.C.K, M.Yu.A, K.R – thermodynamic calculations.

Supplement Data: Click here

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