

Article

Multiphase Open Phase Processes Differential Equations

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Abstract: The thermodynamic approach for the description of multiphase open phase processes is developed based on van der Waals equation in the metrics of Gibbs and incomplete Gibbs potentials. Examples of thermodynamic modeling of the multiphase and multicomponent A^3B^5 systems (In-Ga-As-Sb and In-P-As-Sb) and Na^+ , K^+ , Mg^{2+} , Ca^{2+} / Cl^- , SO_4^{2-} - H_2O water-salt system are presented. Topological isomorphism of different type phase diagrams is demonstrated.

Keywords: open phase process; van der Waals equation; phase equilibrium shift; Gibbs complete and incomplete potential; vector-matrix form

1. Introduction

It is common knowledge that conditions of phase equilibria shifts can be expressed in different mathematical forms, for example, as equality of the intense parameters of state first differentials (temperature, pressure and chemical potentials of components) in equilibrium (α , β) phases: $dT^{(\alpha)} = dT^{(\beta)}$; $dP^{(\alpha)} = dP^{(\beta)}$; $d\mu_i^{(\alpha)} = d\mu_i^{(\beta)}$ [1]. According to these conditions, van der Waals developed the differential equation for the description of phase equilibria shifts in the two-phase binary system [2]. Van der Waals equation allows obtaining the rules and laws characterizing the two-phase equilibrium in one-component and binary systems (Clausius–Clapeyron equation, Gibbs–Kononov law, Gibbs–Roseboom rule, etc.). Storonkin expanded the van der Waals equation for multicomponent systems [3] and developed thermodynamic laws and rules for ternary, quaternary and more component systems (in particular, expanded Clausius–Clapeyron equation for the states characterized by equality of composition in equilibrium phases, van Rijn rule, hetero-azeotropes rule, Schreinemakers rule, etc.). Filippov et al. obtained the vector-matrix form of the van der Waals equation in the Gibbs potential metric [4,5]. Korjinskiy introduced the incomplete Gibbs potentials characteristic in the following set of variables: temperature, pressure, mole numbers and chemical potentials of the components [6].

Filippov et al. developed the vector-matrix form of van der Waals equation in the metric of incomplete Gibbs potential. In addition, they determined that the matrixes of the second concentration derivatives of Gibbs potential are nondegenerated and positively determined according to diffusional criterion of stability [4,5].

Charykova et al. [7] determined the absolute topological isomorphism of different types of phase diagrams (in particular, vapor–liquid equilibria at $T = const$ and $P = const$, fusibility diagrams, solubility diagrams at $T, P = const$, etc.) in the complete and incomplete Gibbs potentials metrics. Phase processes can be divided into two classes:

(i) Close phase processes, when all masses of equilibrium phases coexist in equilibrium during the process. This case is trivial and does not require any additional equations, except classical mass balance equation: $\sum_{i=1}^r [m^{(i)} d\vec{x}^{(i)} + dm^{(i)} \vec{x}^{(i)}] = 0$, where $m^{(i)}, \vec{x}^{(i)}$ – mole number and composition vector of i th phase (in mole fraction concentration scale) and r is a total number of phases.

(ii) Open phase processes, when one or several equilibrium phases are continuously added or removed from the system. Gibbs developed the basic theory and equations for thermodynamic description of such processes [1]. Charykov et al. [8,9] obtained the vector form of differential equations for the description of open phase processes (for example, crystallization process) in the two phase and multiphase polyvariant systems.

The present article is devoted to the development of differential equations for thermodynamic description of different types of open phase processes. In addition, we demonstrate the application of these equations for calculation of open phase processes in multicomponent natural systems.

Van der Waals equations (equations of chemical equilibrium shift) and differential equations of open phase processes, obtained in this article, can be used for the following goals:

- To test corresponding experimental data, concerning phase equilibrium diagrams and open phase processes diagrams; and
- To predict phase equilibrium diagrams and open phase processes diagrams in multicomponent systems, using modeling parameters of non-ideality, determined later from available experimental data in binary and rarely in ternary subsystems.

In the article, the authors consequently consider

- Generalized differential equation of phase equilibrium shifts (van der Waals Equation in Vector-Matrix Form) in the metrics of Gibbs and incomplete Gibbs potentials;
- Differential equations of the open phase processes for two phase and multiphase equilibrium;
- Differential equations of open phase processes in isothermal, isobaric and isothermo-isobaric conditions;
- Non-extreme properties of the driving force parameters in the open phase processes; and
- Some examples of thermodynamic semi-empirical modeling, based on the numerical integration of differential equations of open phase processes in multicomponent semiconductor A^3-B^5 and water–salt systems.

The manuscript is organized as follows: We first describe generalized differential equation of phase equilibrium shifts, van der Waals Equation and common differential equations of open phase processes in isothermal, isobaric and isothermo-isobaric conditions, both in vector-matrix form in the metrics of complete and incomplete Gibbs potentials. The second part of the article presents examples of the application of these differential equations to the description of open phase processes in multicomponent semiconductor (A^3-B^5) and water–salt systems.

2. Generalized Differential Equation of Phase Equilibrium Shifts (Van Der Waals Equation in Vector-Matrix Form)

2.1. Metric of Gibbs Potential

Let us consider the two-phase (α - β) equilibria in the n -component system. In metrics of Gibbs potential, the following parameters are independent variables of phases state: temperature (T), pressure (P) and mole numbers of components (or molar fractions,). The description of the two-phase (α - β) equilibrium shift can be given by the following system of differential van der Waals equations in the vector-matrix form [4,5]:

$$(\vec{x}^{(\beta)} - \vec{x}^{(\alpha)})\hat{G}^{(a)}d\vec{x}^{(a)} = [S^{(a)} - S^{(\beta)} + (\vec{x}^{(\beta)} - \vec{x}^{(\alpha)})\nabla S^{(a)}]dT - [V^{(a)} - V^{(\beta)} + (\vec{x}^{(\beta)} - \vec{x}^{(\alpha)})\nabla V^{(a)}]dP \quad (1)$$

$$(\vec{x}^{(\alpha)} - \vec{x}^{(\beta)})\hat{G}^{(\beta)}d\vec{x}^{(\beta)} = [S^{(\beta)} - S^{(\alpha)} + (\vec{x}^{(\alpha)} - \vec{x}^{(\beta)})\nabla S^{(\beta)}]dT - [V^{(\beta)} - V^{(\alpha)} + (\vec{x}^{(\alpha)} - \vec{x}^{(\beta)})\nabla V^{(\beta)}]dP \quad (2)$$

$$\hat{G}^{(a)}d\vec{x}^{(a)} - \nabla S^{(a)}dT + \nabla V^{(a)}dP = \hat{G}^{(\beta)}d\vec{x}^{(\beta)} - \nabla S^{(\beta)}dT + \nabla V^{(\beta)}dP \quad (3)$$

where $V^{(\tau)}$ and $S^{(\tau)}$ are the molar volumes and entropies of phases ($\tau = \alpha$ or β); $\nabla V^{(\tau)}$ and $\nabla S^{(\tau)}$ are the gradients of these last properties with the concentration $(\partial V^{(\tau)}/\partial x_i^{(\tau)})_{T,P,x_k^{(\tau)} \neq x_{i,n}^{(\tau)}}$ and $(\partial S^{(\tau)}/\partial x_i^{(\tau)})_{T,P,x_k^{(\tau)} \neq x_{i,n}^{(\tau)}}$; $\vec{x}^{(\tau)}$ is a vector, characterizing the state of the figurative point of the τ phase in the concentration space; $d\vec{x}^{(\tau)}$ is a vector characterizing the displacement of $\vec{x}^{(\tau)}$ according to displacement of the two-phase equilibrium; and $\hat{G}^{(\tau)}$ is an operator, corresponding to the matrix of the second derivatives $G_{ij}^{(\tau)}$:

$$G_{ij}^{(\tau)} = \left(\frac{\partial^2 G^{(\tau)}}{\partial x_i^{(\tau)} \partial x_j^{(\tau)}} \right)_{T,P,x_k \neq j,n} \quad (4)$$

where $G^{(\tau)}$ is the molar Gibbs energy potential of the τ phase. According to the phase stability criterion, the matrices of the $\hat{G}^{(\tau)}$ operators and corresponding quadratic bilinear forms are nondegenerate and positively defined. Equations (1) and (2) expressed in the variables of (α) and (β) phases are equivalent. Equation (3) is a condition of phase equilibrium shift.

Parameters $S^{(\alpha \rightarrow \beta)} = [S^{(a)} - S^{(\beta)} + (\vec{x}^{(\beta)} - \vec{x}^{(\alpha)})\nabla S^{(a)}]$ and $V^{(\alpha \rightarrow \beta)} = [V^{(a)} - V^{(\beta)} + (\vec{x}^{(\beta)} - \vec{x}^{(\alpha)})\nabla V^{(a)}]$ have the physical sense of entropy and volume changes in the process of the isothermo-isobaric formation of one mole of β phase from infinitely large mass of α phase.

2.2. Metric of Incomplete Gibbs Potential (Korjinskiy Potential)

Filippov et al. developed van der Waals differential equations (Equations (6)–(8)) in the metric of incomplete Gibbs potential (Korjinskiy potential, see Equation (5)) defined as a function of the following natural parameters—temperature (T), pressure (P), mole numbers of the first k -components (n_1, n_2, \dots, n_k) and chemical potentials of the rest components ($\mu_{k+1}, \mu_{k+2}, \dots, \mu_n$) [6,10]:

$$G_{[k]} = G - \sum_{i=k+1}^n n_i \mu_i = \sum_{i=1}^k n_i \mu_i \quad (5)$$

$$\begin{aligned} (\vec{Y}^{(\alpha)} - \vec{Y}^{(\beta)}) \hat{G}_{[k]}^{(\beta)} d\vec{Y}^{(\beta)} &= [\tilde{S}^{(\beta)} - \tilde{S}^{(\alpha)} + (\vec{Y}^{(\alpha)} - \vec{Y}^{(\beta)}) \nabla \tilde{S}^{(\beta)}] dT - [\tilde{V}^{(\beta)} - \tilde{V}^{(\alpha)} \\ &+ (\vec{Y}^{(\alpha)} - \vec{Y}^{(\beta)}) \nabla \tilde{V}^{(\beta)}] dP + \sum_{q=k+1}^n \left[n_q^{(\beta)} - n_q^{(\alpha)} + (\vec{Y}^{(\alpha)} - \vec{Y}^{(\beta)}) \nabla n_q^{(\beta)} \right] d\mu_q \end{aligned} \quad (6)$$

$$\begin{aligned} (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \hat{G}_{[k]}^{(\alpha)} d\vec{Y}^{(\alpha)} &= [\tilde{S}^{(\alpha)} - \tilde{S}^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \nabla \tilde{S}^{(\alpha)}] dT - [\tilde{V}^{(\alpha)} - \tilde{V}^{(\beta)} \\ &+ (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \nabla \tilde{V}^{(\alpha)}] dP + \sum_{q=k+1}^n \left[n_q^{(\alpha)} - n_q^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \nabla n_q^{(\alpha)} \right] d\mu_q \end{aligned} \quad (7)$$

$$\begin{aligned} &\hat{G}_{[k]}^{(\alpha)} d\vec{Y}^{(\alpha)} - \nabla \tilde{S}^{(\alpha)} dT + \nabla \tilde{V}^{(\alpha)} dP - \sum_{q=k+1}^n \nabla n_q^{(\alpha)} d\mu_q \\ &= \hat{G}_{[k]}^{(\beta)} d\vec{Y}^{(\beta)} - \nabla \tilde{S}^{(\beta)} dT + \nabla \tilde{V}^{(\beta)} dP - \sum_{q=k+1}^n \nabla n_q^{(\beta)} d\mu_q \end{aligned} \quad (8)$$

Evidently, the designations in Equations (1)–(3) are similar to those in Equations (6)–(8), but in the latest case the $G_{[k]}$, S and V functions are referred to one mole of the first k components, and the $\vec{Y}^{(\tau)}$ vectors characterize the position of figurative point of the τ phase (α or β) in the reduced $(k-1)$ -dimensional concentration space:

$$y_i^{(\tau)} = n_i^{(\tau)} / \sum_{j=1}^k n_j^{(\tau)} \quad \left(\sum_{i=1}^k y_i^{(\tau)} = 1 \right) \quad (9)$$

Matrices $G_{[k]ij}^{(\tau)}$ are also nondegenerate, and the corresponding quadratic bilinear forms are positively determined according to Sylvester's criterion [4,5,11].

$$G_{[k]ij}^{(\tau)} = \left(\frac{\partial^2 G_{[k]}^{(\tau)}}{\partial y_i^{(\tau)} \partial y_j^{(\tau)}} \right)_{T,P,y_{l \neq j,k}} \quad (10)$$

Parameters $\tilde{S}^{(\alpha \rightarrow \beta)} = [\tilde{S}^{(\alpha)} - \tilde{S}^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \nabla \tilde{S}^{(\alpha)}]$, $\tilde{V}^{(\alpha \rightarrow \beta)} = [\tilde{V}^{(\alpha)} - \tilde{V}^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \nabla \tilde{V}^{(\alpha)}]$ and $n_q^{(\alpha \rightarrow \beta)} = [n_q^{(\alpha)} - n_q^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)}) \nabla n_q^{(\alpha)}]$ are the changes of entropy, volume and number of moles (of the last $k+1$, $k+2 \dots n$ components), respectively, in the process of the isothermo-isobaric formation of one mole of β phase from infinitely big amount of the α phase taking into account only the masses of the first k components.

2.3. Multiphase Equilibria

Let us consider the equilibrium shift in r -phase ($r \geq 2$). The bottom index (1) refers to the phase containing the maximal number of components. As a rule, the liquid phase consists of the maximal number of components because solid and vapor phases often have the constant composition. For example, in $A^{3-1} - A^{3-2} - \dots - A^{3-N} - B^{5-1} - B^{5-2} - \dots - B^{5-M}$ ($A^{3-I} = Al, Ga, In$, etc.; $B^{5-I} = P, As, Sb, Bi$, etc.), the liquid phase (melt) consists of $(N+M)$ components and the solid solutions (s) only $(N+M-1)$ components due to constraint equation: $\sum_{I=1}^N X_{A^{3-I}}^{(s)} = \sum_{I=1}^M X_{B^{5-I}}^{(s)} = 1/2$.

In this case, the system of van der Waals equations for the equilibria of the phases pairs (1-2; 1-3; 1-4 \dots 1- r) in the variables of (1) phase is the following:

(i) In the metric of Gibbs potential

$$\begin{aligned}(\vec{x}^{(2)} - \vec{x}^{(1)})\hat{G}^{(1)}d\vec{x}^{(1)} &= S^{(1\rightarrow 2)}dT - V^{(1\rightarrow 2)}dP \\(\vec{x}^{(3)} - \vec{x}^{(1)})\hat{G}^{(1)}d\vec{x}^{(1)} &= S^{(1\rightarrow 3)}dT - V^{(1\rightarrow 3)}dP \\&\dots\dots\dots \\(\vec{x}^{(r)} - \vec{x}^{(1)})\hat{G}^{(1)}d\vec{x}^{(1)} &= S^{(1\rightarrow r)}dT - V^{(1\rightarrow r)}dP\end{aligned}\tag{11}$$

(ii) In the metric of incomplete Gibbs potential

$$\begin{aligned}(\vec{Y}^{(2)} - \vec{Y}^{(1)})\hat{G}_{[k]}^{(1)}d\vec{Y}^{(1)} &= \tilde{S}^{(1\rightarrow 2)}dT - \tilde{V}^{(1\rightarrow 2)}dP + \sum_{q=k+1}^n n_q^{(1\rightarrow 2)}d\mu_q \\(\vec{Y}^{(3)} - \vec{Y}^{(1)})\hat{G}_{[k]}^{(1)}d\vec{Y}^{(1)} &= \tilde{S}^{(1\rightarrow 3)}dT - \tilde{V}^{(1\rightarrow 3)}dP + \sum_{q=k+1}^n n_q^{(1\rightarrow 3)}d\mu_q \\&\dots\dots\dots \\(\vec{Y}^{(r)} - \vec{Y}^{(1)})\hat{G}_{[k]}^{(1)}d\vec{Y}^{(1)} &= \tilde{S}^{(1\rightarrow r)}dT - \tilde{V}^{(1\rightarrow r)}dP + \sum_{q=k+1}^n n_q^{(1\rightarrow r)}d\mu_q\end{aligned}\tag{12}$$

Equations (11) and (12) are the systems of (1-2-3 ... r)-phase equilibria shifts in the metrics of different potentials.

3. Differential Equations of the Open Phase Processes

3.1. Two-Phase Processes

Let us formulate the differential equation of the two-phase (α - β) open phase process in vector form. The mass balance equation in the metric of Gibbs potential metric is the following:

$$\vec{x}^{(\alpha)} = (1 - dm^{(\beta)})(\vec{x}^{(\alpha)} + d\vec{x}^{(\alpha)}) + dm^{(\beta)}\vec{x}^{(\beta)}\tag{13}$$

where $m^{(\beta)}$ is a mole number of β -phase formed from one mole of α -phase.

After neglecting the $dm^{(\beta)}d\vec{x}^{(\alpha)}$ second-order small term, one can get the equation:

$$d\vec{x}^{(\alpha)} = -(\vec{x}^{(\beta)} - \vec{x}^{(\alpha)})dm^{(\beta)}\tag{14}$$

where $(\vec{x}^{(\alpha)} - \vec{x}^{(\beta)})$ is a node vector, connecting the figurative points of coexisting equilibrium phases.

The mass balance equation in the metric of Korjinskiy potential is the following:

$$d\vec{Y}^{(\alpha)} = -(\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)})d\tilde{m}^{(\beta)}\tag{15}$$

where $\tilde{m}^{(\beta)}$ is a mole number of β -phase formed from one mole of α -phase (taking into account the first k components), and $(\vec{Y}^{(\alpha)} - \vec{Y}^{(\beta)})$ is quasi-node vector connecting the figurative points of coexisting equilibrium phases in reduced $(k - 1)$ -dimension concentration space.

3.2. Multiphase Processes

Let us formulate the vector form of differential equation of multiphase (1-2- ... -r) open phase process for the description of r-phase equilibrium shifts ($r \geq 2$). In this case, the mass balance equation is the following:

$$\vec{x}^{(1)} = (1 - \sum_{i=2}^r dm^{(i)})(\vec{x}^{(1)} + d\vec{x}^{(1)}) + \sum_{i=2}^r dm^{(i)}\vec{x}^{(i)}\tag{16}$$

one of the equilibrium phases containing the maximal number of components reduces its number up to the value corresponding to the equilibrium phase with decreased number of components (the latest condition leads to extremum of T_P or P_T); and the case when one of the equilibrium phases containing the maximal number of components reduces its number up to the value corresponding to the equilibrium phase with decreased number of components (in the concentration space without solvent molecules). The latest conditions leads to $(\mu_w)_{P,T}$ extremum.

6. Examples of Thermodynamic Modeling

In our opinion, the developed differential equations are very convenient for calculation of open phase processes in real natural or technological systems. To this end, it is enough to determine the dependencies of Gibbs potentials on the parameters of state for all coexisting phases: $G(T, P, \vec{x}), G_{[w]}(T, P, \vec{Y}, n_w)$. Since the standard functions of the components and compounds are well-known and tabulated, the main complicity is determining the excess thermodynamic functions of the solution in different aggregative states. For determination of excess thermodynamic functions, the following semi-empirical models can be used:

- EFLCP model (Excess Functions = Linear Combinations of standard Chemical Potentials) [12,13] for the description of the excess functions in systems containing melts of A^3 - B^5 semiconductors;
- LDM (Lennard–Jones Model) or QRSM model (Quasi Regular Solution Model) [14,15] for the description of excess thermodynamic functions in systems, containing solid solutions of isovalent substitution (for example, in systems containing A^3 - B^5 semiconductors) [12]; and
- classical Pitzer's model [16,17] for the description of excess functions in water–salt systems.

6.1. Two-Phase Open Crystallization in the *In-Ga-As-Sb* and *In-P-As-Sb* Systems at Temperature Decrease

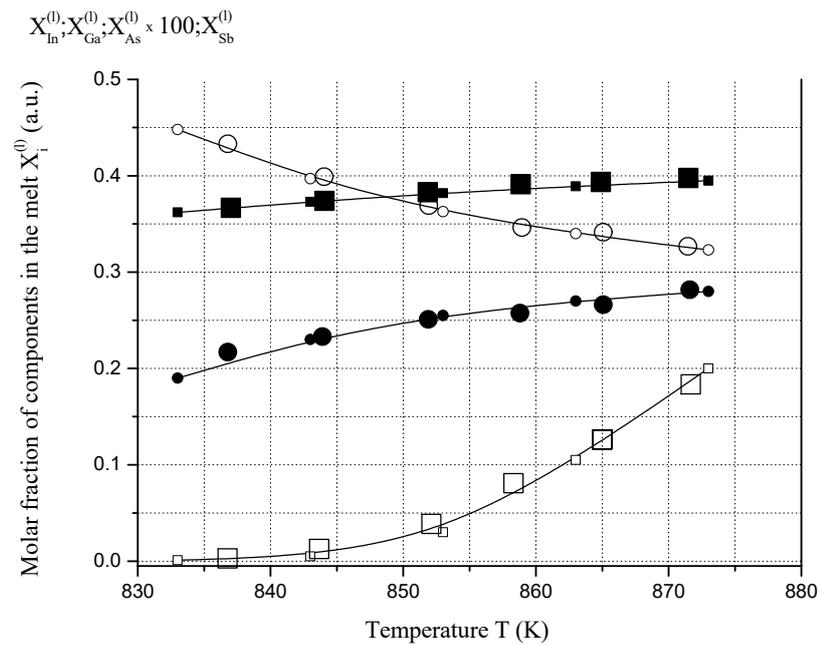
Figure 1 presents open crystallization curves for the *In-Ga-As-Sb* system in the temperature range from 873 to 833 K obtained by LPE (Liquid Phase Epitaxy) from the quaternary melts by crystallization on the *GaSb* monocrystal substrate (1, 0, 0) [18]. The compositions of solid solutions were determined using the indentation plate by X-ray microanalysis in the form of $x_i^{(s)}(d)$ dependencies (d is a plate thickness or depth of indentation). Obtained $x_i^{(s)}(d)$ data were recalculated into the $x_i^{(s)}(T)$ dependencies using experimental data on temperature dependence of the sample mass $m^{(s)}(T)$ (in mole numbers) and Vegard's law for the lattice parameter of solid solution (a):

$$a = 4 \sum_{i=A^3=1}^2 \sum_{j=B^5=1}^2 x_i^{(s)} x_j^{(s)} a_{ij} \quad (45)$$

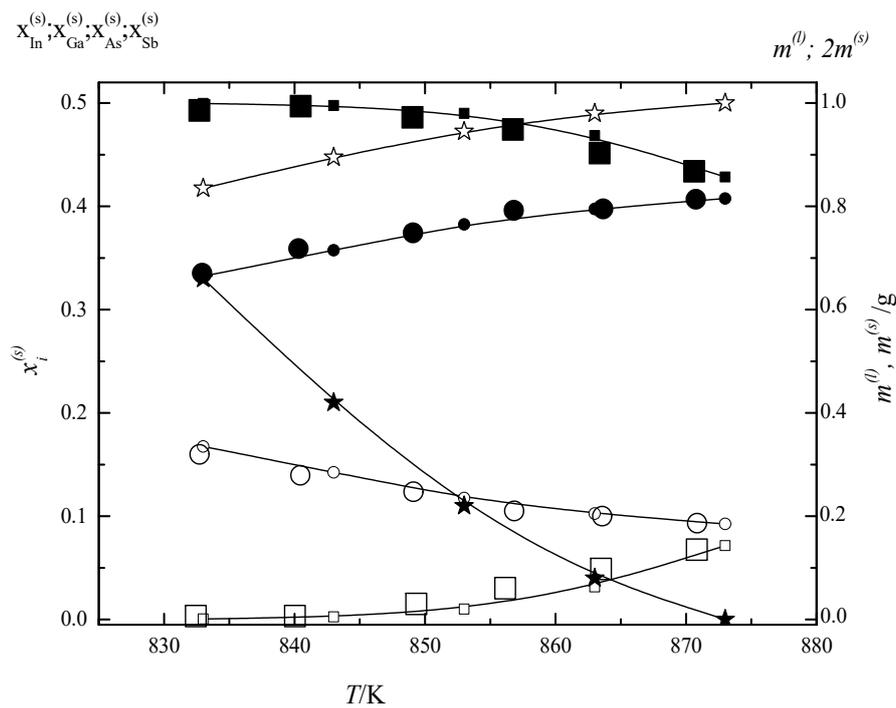
where a_{ij} is a lattice period of the $A_i^3 B_j^5$ compound (*InAs*, *InSb*, *GaAs*, *GaSb*). The molar volumes of solid solution and function d can be calculated as:

$$V^{(s)} = N_a a^3, d = 1/S \int_{T_1}^{T_2} V^{(s)}(T) / (dm^{(s)} / dT)_P dT = 1/S \sum_{i(T_1)}^{i(T_2)} V_i^{(s)}(T) / dm_i^{(s)} / dT \quad (46)$$

where S is a substrate area, i is a number of fragment of the solid solution growth, and $i(T_1)$ and $i(T_2)$ are the first and the last crystallization fragments. In addition, the data on melt composition can be calculated based on experimental data on composition and mass of solid solution using the mass balance equation for all melt components. The same procedure can be used for calculation of the crystallization curves in *In-P-As-Sb* system in the temperature range from 923 to 883 K (Figure 2) [18].



(a)



(b)

Figure 1. Temperature dependences of liquid (a) and solid (b) phases compositions in the In-Ga-As-Sb system: In, ○; Ga, ●; As, □; Sb, ■; little points, calculation; large points, experimental data [18]; masses of equilibrium melt and solid solution, $m^{(l)}$ and $m^{(s)}$ (☆ and ★ in (a)). Conditions of experiment: initial crystallization temperature $T_s = 873$ K, final crystallization temperature $T_f = 833$ K; initial melt mass $m^{(l)_0} = 1.0035$ g; substrate (GaSb) area $S = 1.01$ cm².

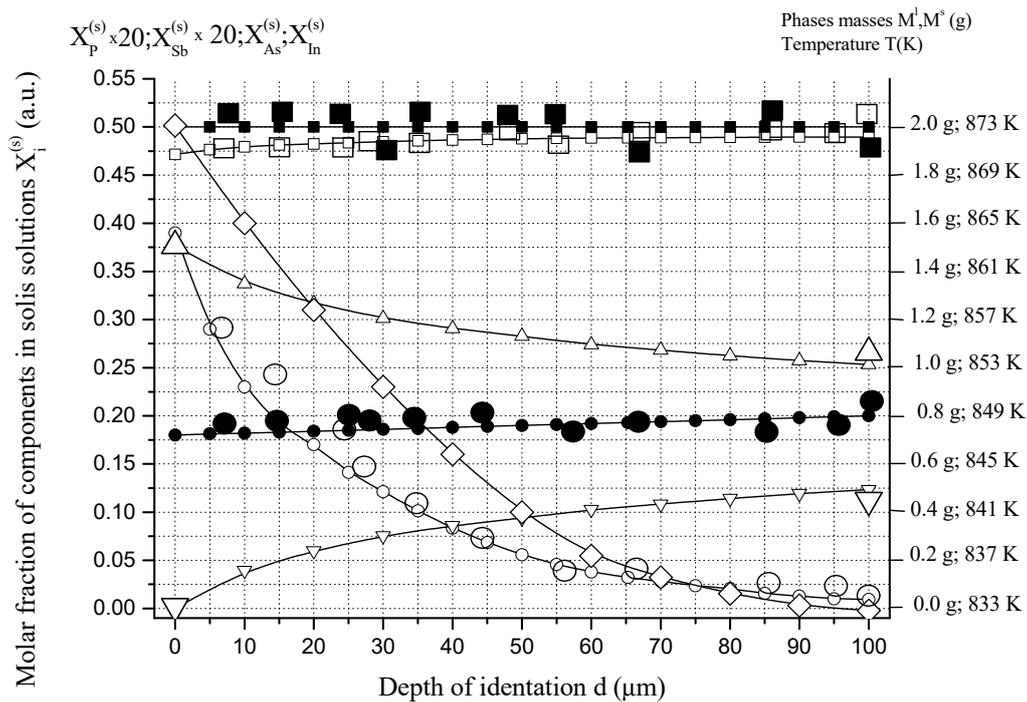


Figure 2. Dependence between the ternary solid solution composition ($x_i^{(s)}$) and indentation depth (d) in the *In-P-As-Sb* system: P, ○; Sb, ●; As, □; In, ■; melt mass, △; solid solution mass, ▽; crystallization temperature, ◇: little points, calculation; large points, experimental data [18]. Conditions of experiment: initial crystallization temperature $T_s = 923$ K, final crystallization temperature $T_f = 883$ K; initial melt mass $m^{(l)}_0 = 1.4009$ g; substrate (*InAs*) area $S = 0.81$ cm².

As standard functions of the components and compounds A^3B^5 in melts and solid phase (standard heats of formation, entropies and isobar heat capacities) are well-known, the parameters of non-ideality or excess thermodynamic functions (EFLCP and MLD (Lennard-Jones Model) show the strongest influence on the accuracy of modeling.

Here and when comparing the calculated and experimental data, deviations between them amounted to up to five relative percent.

6.2. Multiphase Open Crystallization in the $Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} - H_2O$ System at Water Chemical Potential Decrease (Water Evaporation)

Figure 3 presents the open crystallization curves in $Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} - H_2O$ system at 298 K [7]. Chemical potential of water (μ_w)_{P,T} decreases in the range of water activity changing from 0.9416 to 0.3195. In addition, the chemical potential monotonically decreases in the process of open :

$$\mu_w = \mu_w^{(0)} + RT \ln a_w, (\partial \mu_w / \partial n_w)_{T,P,n_i \neq w} > 0 \quad (47)$$

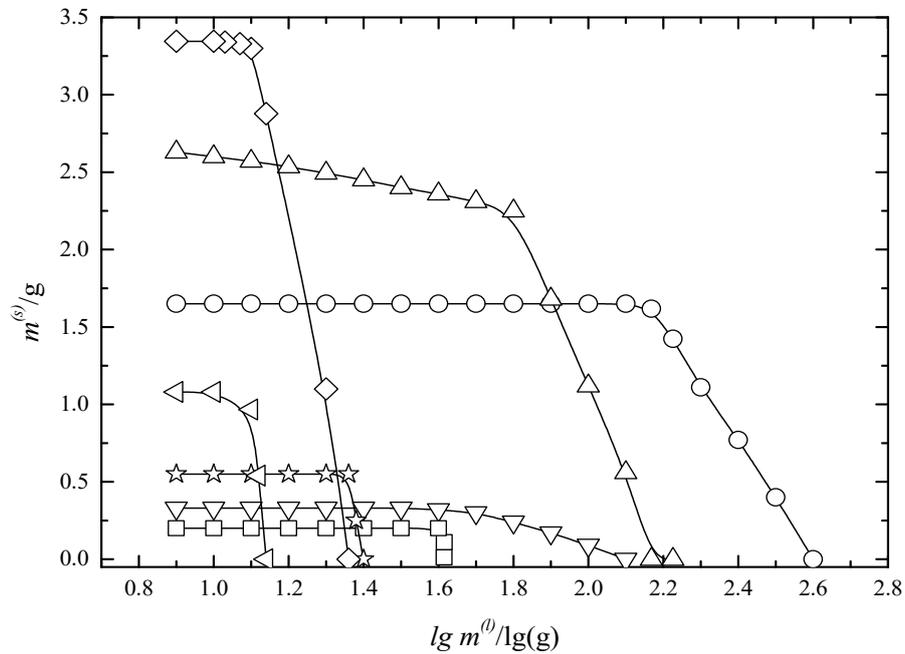
where n_w is a mole number of solvent molecules in liquid solution.

The mole numbers of solid phase in the reduced concentration space (without taking into account the solvent molecules) can be recalculated into $m^{(i)}$ —a function in full concentration space (in mole numbers or grams).

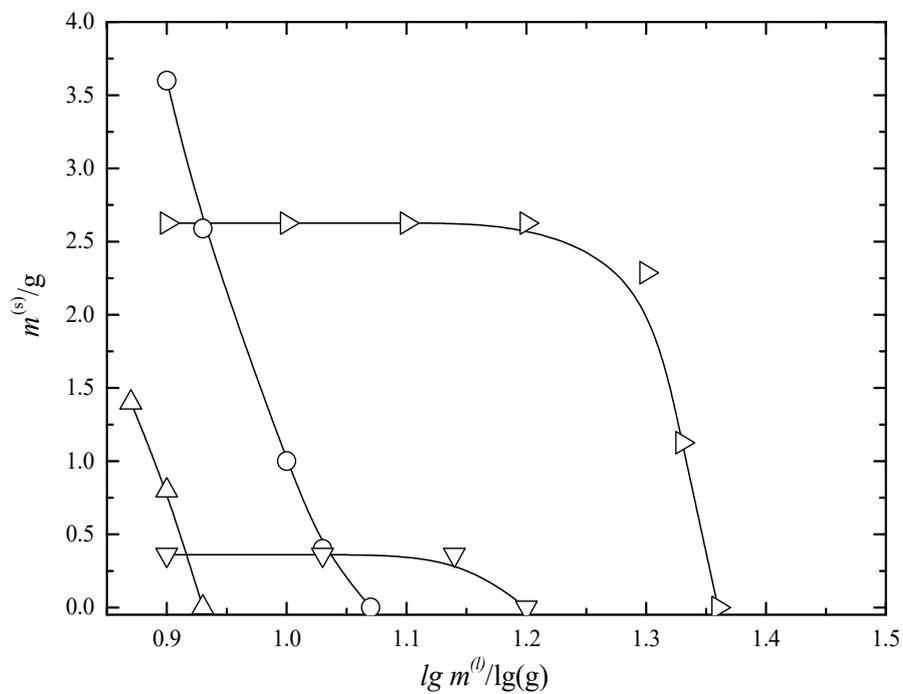
The parameters of non-ideality or excess thermodynamic functions (classical Pitzer model) and thermodynamic potentials of solid phases (in poly-thermal conditions) show the strongest influence on the accuracy of modeling.

The differential equation system in Equation (39) with numerical integration was used for the description of the diagrams in Figure 3. Lines in Figure 3 demonstrate the results of computer modeling of the process of open water evaporation of typical ocean water at 25 °C. Points symbolize states of

phase process change, namely change of the numbers of crystallizing solid phases. In Figure 3a,b, the masses of formed different solid phases and, in Figure 3c, liquid solution composition against logarithm of mass of liquid solution are presented. For the calculation, we used parameters of classical Pitzer equations and solid phases potentials, which are represented in monograph [7].



(a)



(b)

Figure 3. Cont.

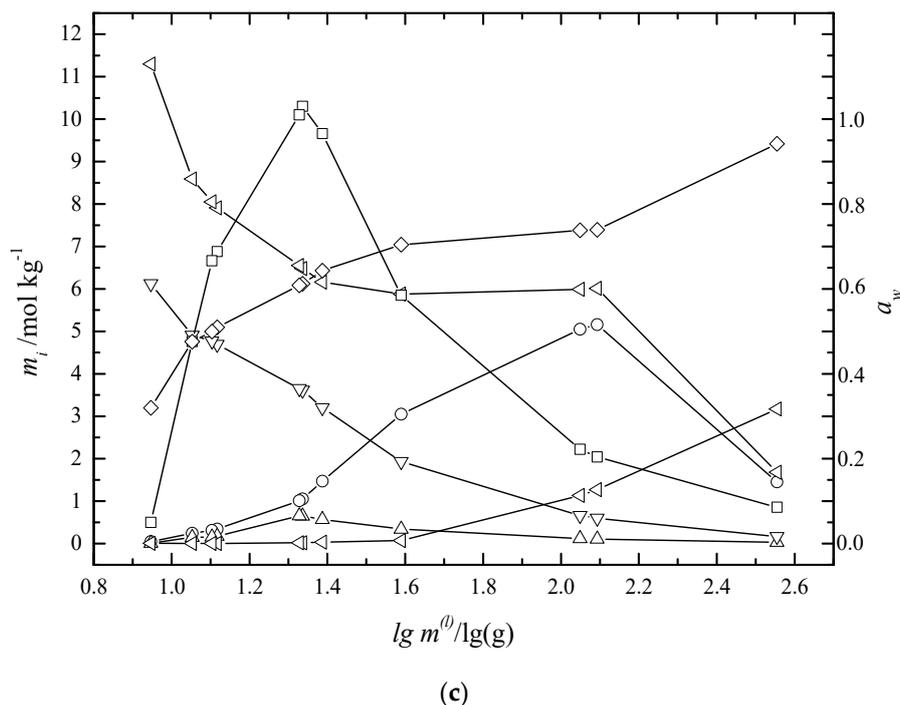


Figure 3. Open crystallization curves in the Na^+ , K^+ , Ca^{2+} , $Mg^{2+} // Cl^-$, $SO_4^{2-}-H_2O$ system. Dependences between the masses of solid phases (a,b) and composition of solution (c), and the solution mass m_i , molality of solution; $m^{(s)}$, mass of the solid phase; open points, calculation; solid points, experimental data. Initial composition of solution ($mol \cdot kg^{-1}$): $m(Na^+) = 0.485$, $m(K^+) = 0.010$, $m(Ca^{2+}) = 0.011$, $m(Mg^{2+}) = 0.056$, $m(Cl^-) = 0.565$; initial solution mass $M^{(l)}_0 = 1000$ g. (a) $CaSO_4 \cdot 2H_2O$, \circ ; $Na_2SO_4 \cdot CaSO_4$, ∇ ; $MgSO_4 \cdot 6H_2O$, \triangleleft , $m^{(s)} \cdot 30$; $NaCl$, \triangle , $m^{(s)} \cdot 0.1$; $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, \square , $m^{(s)} \cdot 10$; $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, \star , $m^{(s)} \cdot 5$; $KCl \cdot MgSO_4 \cdot 3H_2O$, \diamond . (b) $MgSO_4 \cdot 7H_2O$, \triangleright , $m^{(s)} \cdot 15$; $KCl \cdot MgCl_2 \cdot 6H_2O$, \circ , $m^{(s)} \cdot 20$; $MgSO_4 \cdot H_2O$, ∇ , $m^{(s)} \cdot 10$; $MgCl_2 \cdot 6H_2O$, \triangle , $m^{(s)} \cdot 10$. (c) $m(Na^+)$, \circ ; $m(K^+)$, \triangle ; $m(Mg^{2+})$, ∇ ; $m(Ca^{2+}) \cdot 100$, \triangleright ; $m(Cl^-)$, \triangleleft ; $m(SO_4^{2-}) \cdot 10$, \square ; a_w , \diamond .

6.3. Multiphase Open Crystallization in the Na^+ , K^+ , Mg^{2+} , $Ca^{2+} // Cl^-$, $SO_4^{2-}-H_2O$ System at Temperature Decrease

The curves of open crystallization in the Na^+ , K^+ , Ca^{2+} , $Mg^{2+} // Cl^-$, $SO_4^{2-}-H_2O$ system imitating the average ocean water composition in the temperature range from 273 to 243 K are presented in Figure 4a–c as temperature dependences of the solid phase mass, total mass of the system (liquid and solid phases), and composition of liquid phase.

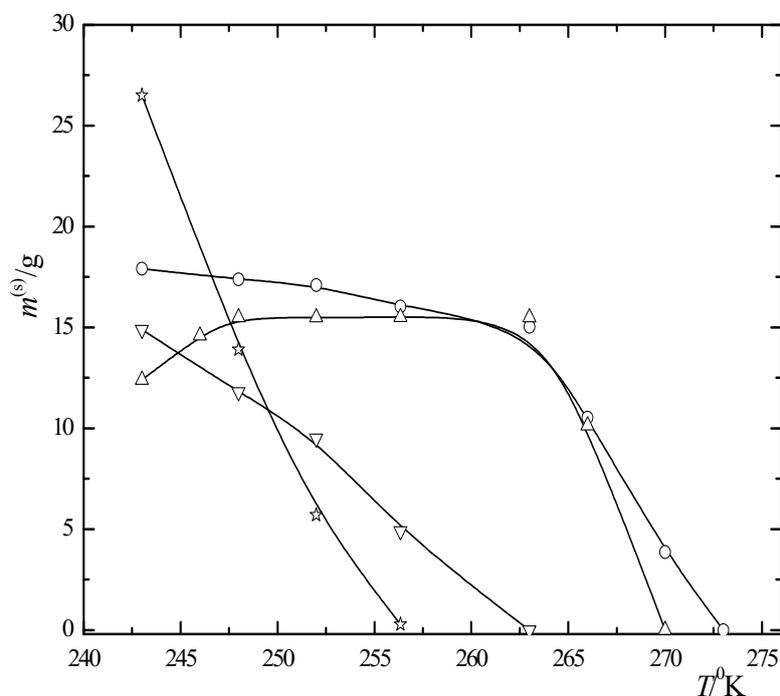
The differential equations system in Equation (25) with numerical integration was used for the description of the diagrams in Figure 4. Lines and open points in Figure 4 demonstrate the results of computer modeling of open crystallization curves in the Na^+ , K^+ , Ca^{2+} , $Mg^{2+} // Cl^-$, $SO_4^{2-}-H_2O$ system during freezing ocean water from 273 to 243 K. Solid points in Figure 4b,c symbolize literature experimental data. In Figure 4a, the masses of formed different solid phases, in Figure 4b, total mass of solid phases and mass of liquid solution, and, in Figure 4c, liquid solution composition against temperature are presented. For the calculation, we also used parameters of classical Pitzer equations and solid phases potentials temperature dependencies, which are represented in monograph [7]. One can see good agreement between literature experimental and calculated data. Here and everywhere below when comparing the calculated and experimental data (if any), deviations between them amounted to up to 10 relative percent.

The developed thermodynamic approach and the algorithm for calculation of open phase processes is also valid for the description of metastable equilibrium characterized by stability against infinitely small changes of state and unstable against finite changes of state. In our case, the equilibrium in the Na^+ , K^+ , Ca^{2+} , $Mg^{2+} // Cl^-$, $SO_4^{2-}-H_2O$ system is metastable because such stable

phases as $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ cannot be formed. This type of crystallization is typical for quick water evaporation, which occurs during the ocean water evaporation in the conditions of shallow basins under the action of sunrays (see Figure 5), data are represented in [7].

At the same time, the stability criterion against the infinitely small changes of state (diffusional stability criterion) must be valid. In the opposite case, the determinants of bilinear forms and minors of its main diagonals corresponding to $\hat{G}^{(i)}$, $\hat{G}_{[k]}^{(i)}$ operators and $\Delta_{Gr}^{(r-1)}$, $\tilde{\Delta}_{Gr}^{(r-1)}$ determinants change the sign.

The differential equations system in Equation (39) with numerical integration was used for the description of the diagrams in Figure 5. Lines and open points in Figure 5 demonstrate the results of computer modeling of the process of metastable open water evaporation of typical ocean water at 298 K. Solid points in Figure 5 symbolize literature experimental data. In Figure 5, the masses of formed different solid phases against logarithm of mass of liquid solution are presented. For the calculation, we used parameters of classical Pitzer equations and solid phases potentials, which are represented in monograph [7].



(a)

Figure 4. Cont.

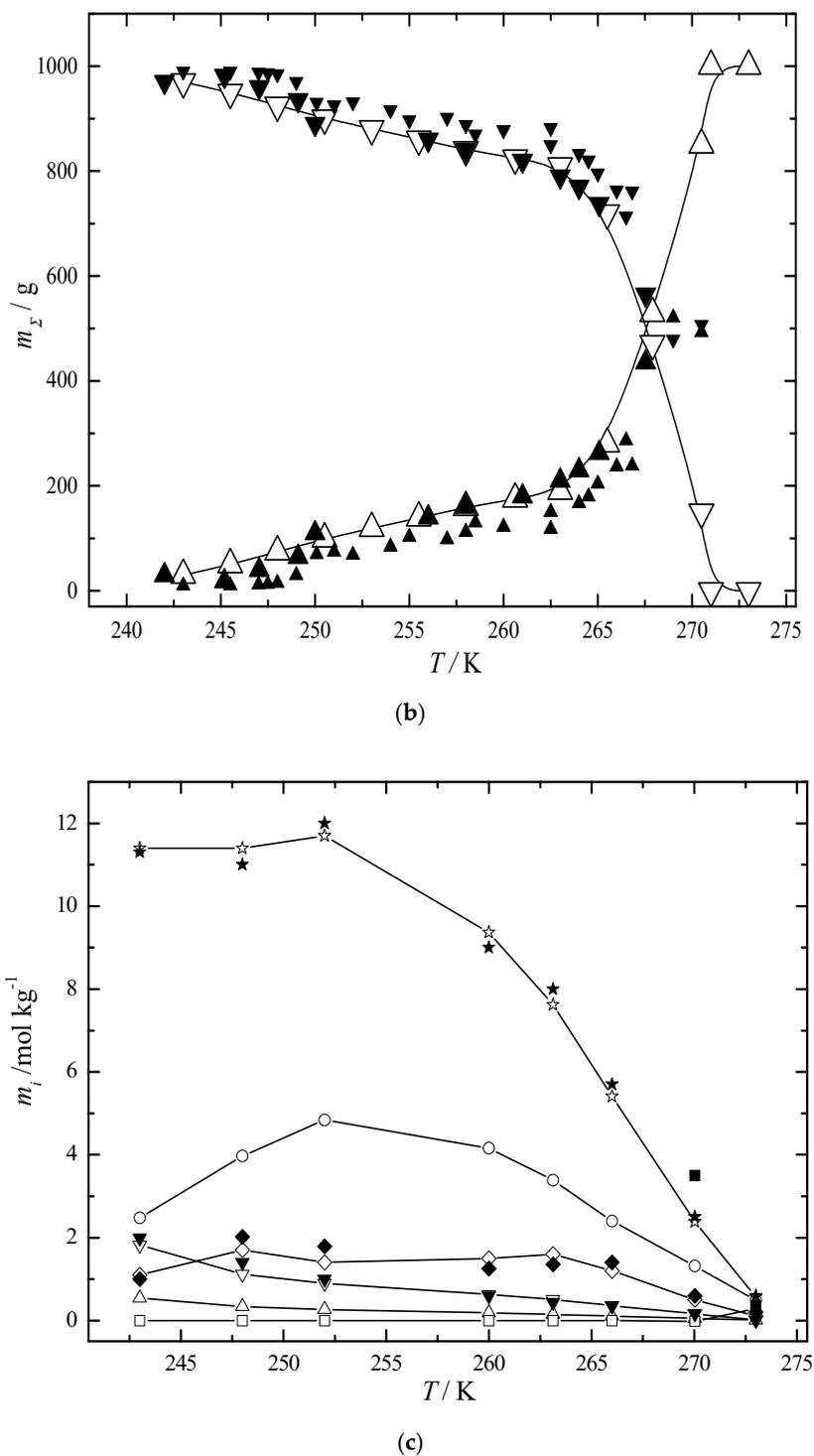


Figure 4. Open crystallization curves in the Na^+ , K^+ , Ca^{2+} , Mg^{2+} // Cl^- , SO_4^{2-} - H_2O system during freezing from 273 to 243 K. Temperature dependences of the solid phase masses (a); total mass of the system (liquid and solid phases) (b); and composition of liquid phase (c). m_i , molality of solution; $m^{(s)}$, mass of the solid phase; $m^{(l)}$, mass of the liquid phase; m_{Σ} , total mass of the system (liquid and solid phases) open points, calculation; solid points, experimental data. Initial composition of solution (mol·kg⁻¹): $m(\text{Na}^+) = 0.485$, $m(\text{K}^+) = 0.010$, $m(\text{Ca}^{2+}) = 0.011$, $m(\text{Mg}^{2+}) = 0.056$, $m(\text{Cl}^-) = 0.565$, $m(\text{SO}_4^{2-}) = 0.029$; initial solution mass $M^{(l)}_0 = 1000$ g. (a) H_2O (ice), \circ , $m^{(s)} \cdot 0.02$; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, \triangle ; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ∇ , $m^{(s)} \cdot 10$; $\text{NaCl} \cdot 2\text{H}_2\text{O}$, \star . (b) Values of the liquid phase mass ($m^{(l)}$), \triangle , \blacktriangle ; values of the total mass (m_{Σ}), ∇ , \blacktriangledown ; $m(\text{Na}^+)$, \circ , \bullet ; $m(\text{K}^+)$, \triangle , \blacktriangle ; $m(\text{Mg}^{2+})$, ∇ , \blacktriangledown ; $m(\text{Ca}^{2+}) \cdot 100$, \diamond , \blacklozenge ; $m(\text{Cl}^-)$, \star , \blackstar ; $m(\text{SO}_4^{2-}) \cdot 10$, \square , \blacksquare .

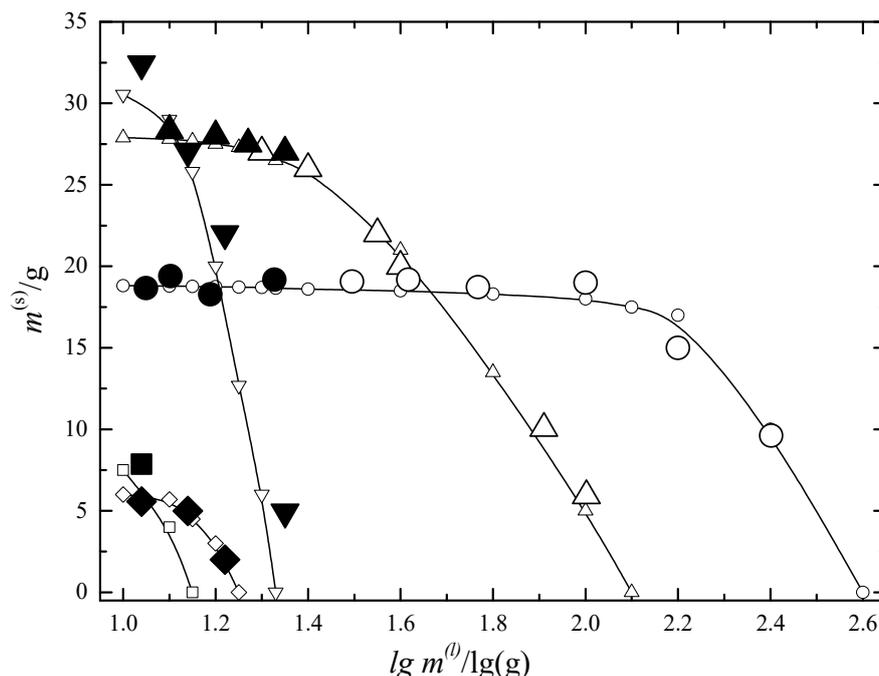


Figure 5. Open crystallization curves in the Na^+ , K^+ , Ca^{2+} , Mg^{2+} // Cl^- , SO_4^{2-} - H_2O system during water evaporation at 298 K. Dependence between the solid phase masses ($m^{(s)}$) and solution mass ($m^{(l)}$). Open points, calculation; solid points, experimental data; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, \circ , \bullet , $m^{(s)} \cdot 10$; NaCl , \triangle , \blacktriangle ; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, ∇ , \blacktriangledown , $m^{(s)} \cdot 10$; KCl , \diamond , \blacklozenge , $m^{(s)} \cdot 10$; $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, \square , \blacksquare , $m^{(s)} \cdot 10$. Initial composition of solution ($\text{mol} \cdot \text{kg}^{-1}$): $m(\text{Na}^+) = 0.485$, $m(\text{K}^+) = 0.010$, $m(\text{Ca}^{2+}) = 0.011$, $m(\text{Mg}^{2+}) = 0.056$, $m(\text{Cl}^-) = 0.565$, $m(\text{SO}_4^{2-}) = 0.029$, initial solution mass $M^{(l)}_0 = 1000$ g.

7. Conclusions

Based on generalized van der Waals equations in the metrics of complete and incomplete Gibbs potentials, we proved the topological isomorphism of phase diagrams, namely liquid–vapor in the $P(\vec{x})$ and $T(\vec{X})$ variables at constant T and P , liquid–solid in the $T(\vec{X})$ variables at $P = \text{const}$ and liquid–solid in the $Y_i - Y_j$ variables at $P, T = \text{const}$. The paper presents thermodynamic approach for the description of different types of open phase processes. Additionally, we demonstrated the validity of developed equations for the calculation of open phase processes by the examples of the several multicomponent model systems. The developed approach has, in our opinion, some benefits:

- It is most common and does not depend of the type of phase process or components number.
- It is not recursive and gives unidirectional motion in the direction of action of thermodynamic forces of phase process.
- The algorithm is easy to program, because, in the region of diffusional stability, we are always dealing with convex functions and positively determined (according to Sylvester's theorem) bilinear forms in our differential equations. The vector-matrix form of writing equations in this case is, in our opinion, the most compact and convenient for the calculation and analysis.
- The main novelty of this work is the following not very obvious result: in the opinion of the authors, for the first time, the equations systems of phase processes have been deduced, where masses of phases are natural parameters of state, absolutely the same as classical parameters: temperature, pressure, components molar numbers, etc.

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