Original articles

A universal algorithm for the calculation of vapor-liquid equilibrium diagrams in quasi-simple multicomponent systems

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Abstract

The purpose of the study was to consider isothermal vapor-liquid diagrams of quasi-simple systems and to develop a universal algorithm for the calculation of isothermal vapor-liquid diagrams of these systems independent of the type of valence of the electrolyte, the number of components in the system, and the types of solid solutions. The suggested analogues of the three Gibbs–Konovalov and Gibbs–Roozeboom laws are true when moving along the univariant equilibrium lines on the solubility diagrams of systems with a random number of components.

The study did not involve any experiments. The suggested algorithm was applied for the description of solubility (solid-liquid) diagrams and vapor-liquid equilibrium diagrams of three- and four-component systems with one, two, or three volatile components. In all the cases, the results of thermodynamic first-principles calculations agreed well with the experimental data presented in the literature.

Both the experimental data presented in the literature and the results of the thermodynamic first-principles calculation performed by the authors are also in good agreement with the suggested analogues of the Gibbs–Konovalov and Gibbs–Roozeboom laws.

Keywords: Zdanovskii's rule, Quasi-simple systems, Vapor-liquid equilibrium diagrams, Partial molar Gibbs energy, Analogues, Gibbs–Konovalov's laws, Gibbs–Roozeboom rules

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1. Introduction

1.1. Main thermodynamic properties of quasi-simple systems

We shall start by introducing the main definitions. Water-salt systems with three or more components (or, in the general case, solvent-solute systems) comply with the so-called Zdanovskii's rule, if isoactivates of the solvent (hereinafter, water – W) are line segments ($n = 3$), plane sections ($n = 4$), or hyperplane sections ($n \geqslant 5$) [1–6]. Section 1.1 of the article is largely based on the terms used in [6]. The article considers isothermal–isobaric conditions (T, P = const). Water isoactivates (a_w = const) are isopotentials (μ_w = const; μ_w is the chemical potential), isobars of partial pressures of water (P_w = const), and isotherm-isobars of a two-phase vapor-liquid equilibrium (l–v) in the region of homogeneous liquid solutions at the same time [1-6]. The equation of the isoactive line divided into segments for a ternary system complying to Zdanovskii's rule is mathematically expressed by the following relation [1, 3, 4, 6]:

$$m_1 / m_1^0 + m_2 / m_2^0 = 1, \quad (1)$$

where: m_i и m_i^0 is the molality of the i-th component of a ternary and a binary system with the same value of μ_W, respectively. When dealing with a random n-component system, the equation of the isoactive hyperplane is presented as follows:

$$\sum_{i=1, i \neq W}^{n-1} m_i / m_i^0 = 1 ; \quad (2)$$

or:

$$\sum_{i=1, i \neq W}^{n-1} Y_i = 1; \quad Y_i = m_i / m_i^0. \quad (3)$$

It is important that the isopotentials of other (i.e. salt) components are not line segments or hyperplane sections. In particular, they are crystallization curves of these anhydrous components on the solubility diagrams of ternary systems and cannot be linear by nature.

Hereinafter, in order to avoid ambiguity, we will refer to systems as being **quasi-simple** if the **isoactivates** of at least one component are **linear**. In this case, the properties of systems with three or more components are determined by the properties of their binary subsystems. This is accounted for by the Gibbs-Duhem equation and the conditions of cross product derivation for the liquid phase under isothermal–isobaric conditions [4, 7-9]:

$$SdT - VdP + \sum_{i=1}^{n} n_i d\mu_i = 0 \quad (4)$$

or when $T, P = const$:

$$\sum_{i=1}^{n} n_i d\mu_i = 0, \quad (5)$$

$$\frac{\partial^2 G}{\partial n_i \partial n_j} = \frac{\partial^2 G}{\partial n_j \partial n_i} \quad (6)$$

or when $T, P = const$:

$$\partial \mu_i / \partial n_j = \partial \mu_j / \partial n_i. \quad (7)$$

Thus, in particular, excess thermodynamic functions of multi-component liquid phases (activity of the components – a_i, activity coefficients – γ_i, water osmotic coefficients – ϕ), as well as equilibrium diagrams (l–v) and (s–l) of multi-component systems should be calculated based on the data regarding the thermodynamic functions of their binary subsystems. The main question can be formulated as follows: "Which unique properties of thermodynamic potentials of a phase of variable composition, i.e. a liquid (in our case, they are the Gibbs energy – G or partial potentials – Korzhinsky's potentials [4, 10] – $G^{[W]}$), make a system quasi-simple?". This question can be answered by determining the type of functional dependence of excess thermodynamic functions on the composition of multi-component systems.

Let's briefly review the main points presented in [6]. Let's consider an n-component system: 1–2–3...n–1–W (W is a solvent (water), components 1, 2, 3... n-1 are dissolved electrolytes (salts)) with T, P = const. Let's introduce the partial Gibbs energy [4, 10–12]:

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$$G^{[W]} = G - n_W \mu_W = \sum_{i=1, i \neq W}^{n-1} n_i \mu_i, \qquad (8)$$

where $G^{[W]}$ is the partial Gibbs energy, μ_i is the chemical potential of the i-th solute; μ_w is the chemical potential of water. $G^{[W]}$ is characteristic for the set of variables (T, P, n_i ($i \leqslant n-1$), μ_W). Let's now consider the quasi-average partial molar Gibbs energy calculated for 1 mole of solutes – $G^{(W)}$:

$$G^{(W)} = \sum_{i=1, i \neq W}^{n-1} Z_i \mu_i, \qquad (9)$$

where: Z_i is the mole fraction of the i-th solute in the concentration space without solvents:

$$Z_j = \frac{n_j}{\sum_{i=1, i \neq W}^{n-1} n_i}; \quad \sum_{i=1, i \neq W}^{n-1} Z_i = 1 \ . \qquad (10)$$

When $T, P = $ const, $G^{(W)}$ is characteristic for the set of variables ($Z_1, Z_2, ..., Z_{n-2}$, μ_W).

Let's introduce the function $\Delta G_{mix}^{(W)}$, which reflects changes in the average partial molar Gibbs energy when mixing ($n-1$) binary solutions ($i-W$), each of which contains Z_i moles of the i-th component [6]. Let all the mixed binary solutions have the same chemical potential of the solvent (i.e. are isopiestic), $\mu_W^{(1-W)} = \mu_W^{(2-W)} = ... = \mu_W^{(n-1-W)} = const$. Let's assume that after mixing, the chemical potential of the solvent in the resulting multi-component system remains the same, $\mu_W^{(mult)} = const$ i.e. the system complies with Zdanovskii's rule. Then function $\Delta G_{mix}^{(W)}$ no longer depends on μ_w but rather on the variables of the composition – Z_i: $\Delta G_{mix}^{(W)}(Z_1, Z_2 ... Z_{n-2})$ [6]. Obviously, in the general case:

$$\frac{\Delta G_{mix}^{(W)}}{RT} = \sum_{i=1}^{n-1} Z_i \left(\ln a_i^{(mult)} - \ln a_i^0 \right), \qquad (11)$$

where: $a_i^{(mult)}$ is the activity of the i-th solute after mixing; a_i^0 is the activity of the i-th solute in the binary system ($i-W$) with the same value of μ_w before mixing [6].

Let's assume that **in quasi-simple systems, the function $\Delta G_{mix}^{(W)}$, corresponding to the mixing of binary solutions (i-W) with the same μ_W, provided that μ_W remains unchanged after mixing, is only determined by the entropy of ideal mixing of binary solutions** or [6]:

$$\frac{\Delta G_{mix}^{(W)}}{RT} = \sum_{i=1}^{n-1} Z_i \ln Z_i . \qquad (12.1)$$

In other words, the excess partial Gibbs free energy of the mixed isopiestic binary solutions ($\Delta G_{mix}^{(W)-ex}$) should be zero:

$$\frac{\Delta G_{mix}^{(W)-ex}}{RT} = 0 . \qquad (12.2)$$

By comparing equations (11) and (12.1) we obtain:

$$\ln a_i^0 + \ln Z_i = \ln a_i^{(mult)} \ (\text{при } \mu_W = const), \qquad (12.3)$$

$$\ln m_i = \ln Z_i + \ln m_i^0, \qquad (13)$$

where: m_i^0 is the molality of the i-th component in the binary solution (before mixing) with constant μ_w; m_i is the molality of the i-th component in the multi-component solution (after mixing) with the same value of μ_w.

In [6], the main equations (12.1) – (12.3) are substantiated in a different way. Let's accept the classical definition of the number of components in a system (n) as a number of ion and molecular forms in the system, whose masses can change independently [4, 6, 9]. Let's assume that the studied system is quasi-simple. Let the chemical potential of the solvent be $\mu_w = const$. Then binary solutions ($i-W$) with identical μ_w can be considered to be **new individual components.** If, with the same μ_w, these components are mixed as components of an ideal solution, then equations (12.1)–(12.3) are true.

[6] presents the results of the first-principles calculation of equations (12, 13) based on the data regarding the corresponding binary subsystems of the solubility diagrams of three- and four-component systems with crystallization of anhydrous salt components, their crystalline hydrates, ternary compounds of constant compositions, and solid solutions with isovalent substitutions. In all the cases, the calculations agreed well with the experimental data presented in the literature.

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1.2. Calculation of vapor-liquid equilibria of quasi-simple systems

The article focuses on first-principles calculation of vapor-liquid equilibrium diagrams of three- and more component systems with volatile components based on equations (12, 13) and the data regarding their binary subsystems.

Let the chemical potential or activity of water be constant ($\mu_w = const$; $\ln a_w = const$).

According to Henry's law, for the partial vapor pressure of a volatile component of a multi-component system (hereinafter, assuming that the vapor phase is ideal) the following is true [7, 9, 13]:

$$\ln P_i = \ln a_i^{(mult)} + \ln K_{H,i}^m , \qquad (14.1)$$

where: P_i is the partial pressure of the i-th volatile component (mm Hg), $a_i^{(mult)}$ is the activity of the i-th component on the molality scale, and $K_{H,i}^m$ is the Henry's law constant of the i-th component on the molality scale. Or, taking into account (12.3):

$$\ln P_i = \ln a_i^0 + \ln Z_i + \ln K_{H,i}^m \text{ (при } \mu_W = const), (14.2)$$

where: a_i^0 is the activity of the i-th solute in the binary system ($i-W$) with the same μ_w before mixing [6].

The partial pressure of the solvent P_w is determined according to Raoult's law [7, 9, 13]:

$$\ln P_W = \ln a_W + \ln P_W^{(0)} , \qquad (14.3)$$

where $P_W^{(0)}$ is the vapor pressure above the pure solvent under specific conditions (mm Hg). For instance, with water being the solvent, at 25 °C $P_W^{(0)} = $ = 23.76 mm Hg.

Thus, according to Dalton's law, the total vapor pressure above the solution is P_{sum}, [7, 9, 13]:

$$P_{sum} = \sum_{i=vc} a_i^0 Z_i K_{H,i}^m + a_W P_W^{(0)} , \qquad (14.4)$$

where all the volatile components except for the solvent are summarized. The composition of the solution (m_i) is set by equation (13), based on the data regarding binary isopiestic concentrations (m_i).

## 2. Binary systems HCl – H_2O and HBr – H_2O at 25 °C

This section, though not entirely within the scope of the study, is still important, because it demonstrates the accuracy of the calculation of partial pressures of the components performed by means of a classical model of electrolyte solutions used to describe binary systems, namely the Pitzer model [14, 15] with three and four parameters. As a result, we selected two binary systems with two volatile components: a solvent ($W = H_2O$) and a volatile acid, HCl – H_2O, HBr – H_2O at 25 °C. The data regarding the binary Pitzer parameters is presented in Table 1. We should note that the said parameters quite accurately describe the concentration dependence of the water osmotic coefficients on the molality of the binary solutions $\varphi(m)$ almost over the whole concentration range m = 0÷16 mol/kg H_2O, including the region of azeotropes (Az), where the vapor pressure is low ($P_T^{Az} = \min$). The corresponding Henry constants ($K_{H,HCl}^m ; K_{H,HBr}^m$) are given in Table 2. Fig. 1 and 2 present the results of calculations and the experimental data regarding the partial pressures of halogen hydracids and water and the total vapor pressure above the solutions studied in [16, 17]. The figures show that the experimental and calculated data are in good agreement, including in the region of binary azeotropes – Az_i.

Table 1. Binary Pitzer parameters at 25 °C

System	Binary parameters (r.u.)					
	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^φ	α_1	α_2
NaCl–H_2O	0.0765	0.2664	0	0.00124	2.0	–
KCl–H_2O	0.0484	0.2122	0	-0.00084	2.0	–
LiCl–H_2O	0.27909	1.5093	−0.78110	-0.00765	2.0	1.0
LiNO$_3$–H_2O	0.09642	0.03872	0.02704	-0.01010	2.0	−0.4
HCl–H_2O	0.1769	0.2972	0	0.00072	2.0	–
HBr–H_2O	0.2259	0.1372	0.0289	-0.00167	2.0	1.0

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Table 2. Henry constants (on molality scale) for systems HCl – H_2O, HBr – H_2O at 25 °C

System	HCl–H_2O	HBr–H_2O
K_H^m (mm Hg)	$1.99 \cdot 10^{-4}$	$4.04 \cdot 10^{-6}$
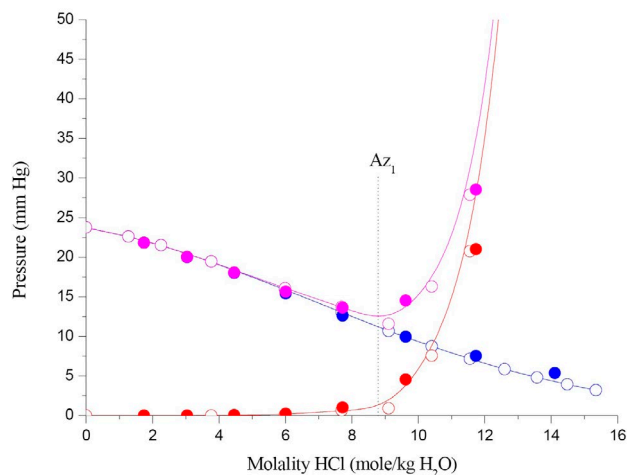
Fig. 1. The data calculated based on the Pitzer equations (lines and open circles) and the experimental data [16] (solid circles) regarding the concentration dependence of the pressures: H_2O (blue), HCl (red), and total (violet). Az_1 – azeotrope
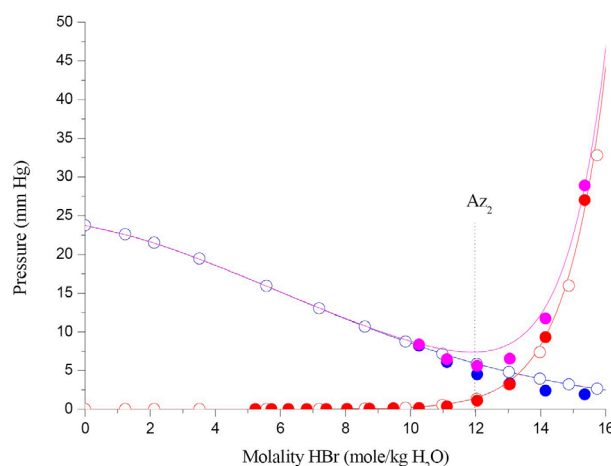
Fig. 2. The data calculated based on the Pitzer equations (lines and open circles) and the experimental data [17] (solid circles) regarding the concentration dependence of the pressures: H_2O (blue), HBr (red), and total (violet). Az_2 – azeotrope

3. Ternary systems with one volatile component – the solvent (for instance, the LiCl – $LiNO_3$ system) at 25 °C

This section considers a system with one volatile component, namely the LiCl – $LiNO_3$ system at 25 °C. The system is quite trivial. Its equilibrium diagram is represented by a set of linear isoactivates of water. Therefore, we assume that the system complies with Zdanovskii's rule over the whole concentration range. The calculated and experimental isoactivates of water in the studied system are presented in Table 3 and Fig. 3. The experimental data regarding the water activity was obtained by means of the isopiestic method using a variation of Resnik's measurement unit [18]. Binary solutions of the LiCl – H_2O system were used as reference solutions. The solubility was calculated based on the data regarding the binary subsystems using an algorithm of calculation of solubility diagrams suggested in [6]. Fig. 3 shows that the calculated data on the isoactivates of water agrees well with the experimental data. In order to determine the degree of compliance of the LiCl – $LiNO_3$ – H_2O system at 25 °C with Zdanovskii's rule, we
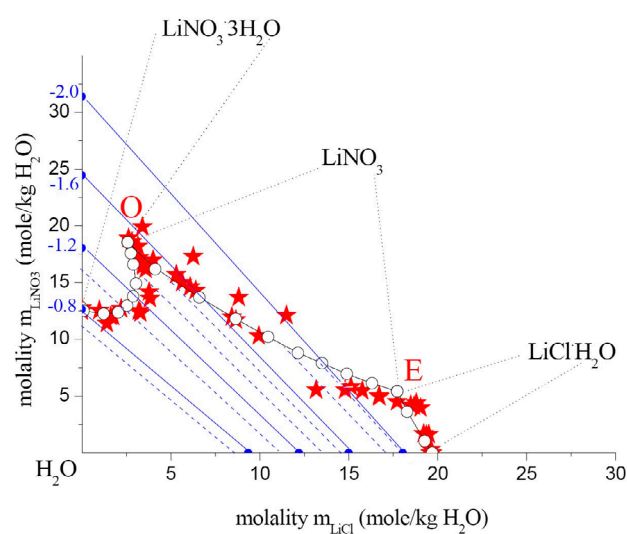

Fig. 3. Solubility diagram of the LiCl – $LiNO_3$ – H_2O system at 25 °C (open circles and lines – calculation results, red stars – experimental data [19], blue solid lines – calculated water isoactivates, $\ln a_W$ values are shown in blue, blue dotted lines – experimental data obtained by the authors). According to the general classification of invariant points [20, 21], point O is a so–called through point, corresponding to the saturation with two different crystalline hydrates of one salt component, and point E is eutonic

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Table 3. Dependence of osmotic coefficients on the solution composition in the LiCl – LiNO$_3$ – H$_2$O system at 25 °C

m_{LiNO_3} (mol/kg H$_2$O)	m_{LiCl} (mol/kg H$_2$O)	φ_{H_2O}	m_{LiNO_3} (mol/kg H$_2$O)	m_{LiCl} (mol/kg H$_2$O)	φ_{H_2O}
ln $a_W = -0.6999$			ln $a_W = -1.0674$		
11.36	0.00	1.71	16.55	0.00	1.79
9.50	1.39	1.78	13.62	1.99	1.90
8.02	2.51	1.84	11.34	3.56	1.99
6.65	3.55	1.90	9.28	4.95	2.08
5.34	4.54	1.96	7.37	6.27	2.17
4.30	5.33	2.01	5.89	7.36	2.14
3.26	6.13	2.06	4.43	8.31	2.33
2.39	6.78	2.11	3.21	9.11	2.41
1.48	7.47	2.17	1.98	9.95	2.49
0.65	8.10	2.22	1.71	10.11	2.56
0.00	8.59	2.26	0.00	11.29	2.60
ln $a_W = -1.3490$			ln $a_W = -1.5055$		
16.88	2.47	1.93	18.75	2.74	1.94
13.90	4.36	2.05	15.39	4.83	2.06
11.28	6.03	2.16	12.42	6.64	2.19
8.88	7.57	2.28	9.76	8.31	2.31
7.05	8.73	2.37	7.71	9.59	2.41
5.26	9.87	2.47	4.14	11.75	2.63
3.81	10.80	2.56	2.53	12.76	2.73
2.33	11.73	2.66	0.00	14.31	2.92
0.00	13.23	2.83	ln $a_W = -1.8461$		
ln $a_W = -1.6741$			7.18	12.45	2.61
8.64	10.14	2.47	4.84	13.84	2.68
6.59	11.43	2.58	4.29	14.18	2.77
5.37	12.18	2.65	2.93	15.05	2.85
3.95	13.06	2.73	1.45	15.91	2.95
2.70	13.84	2.81	0.00	16.80	3.05
1.34	14.70	2.90			
0.00	15.54	2.99			
ln $a_W = -1.9976$					
4.63	15.31	2.78			
3.16	16.18	2.87			
1.56	17.13	2.97			
0.00	18.06	3.07			

presented the deviations of the water isoactivates from linearity $\Delta_{Zd} = 1 - m_{LiNO_3} / m_{LiNO_3}^0 - m_{LiCl} / m_{LiCl}^0$ as a function of the Janecke index of LiNO$_3$ – $Y_{LiNO_3} = m_{LiNO_3} / (m_{LiNO_3} + m_{LiCl})$ over the whole array of experimental data (Fig. 4). Fig. 4 shows that for all the 55 experimental points, except for one, deviations from Zdanovskii's rule are very insignificant (≤ 0.002), which demonstrates

the accuracy of the isopiestic experiment. The thermodynamic potentials of the solid phases required for the calculation of the solubility diagrams of the LiCl – LiNO$_3$ – H$_2$O system at 25 °C are presented in Table 4. The table also demonstrates the thermodynamic potentials – ln SP (SP – solubility product of the solid phase) of all the other solid phases in the subsequent

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Table 4. Thermodynamic potentials of solid phases (ln SP) at 25 °C

Solid phase	ln SP	Solid phase	ln SP	Solid phase	ln SP
NaCl	3.65	LiCl·H_2O	12.13	KCl	2.09
LiNO$_3$	9.08	LiNO$_3$·3H_2O	4.73		

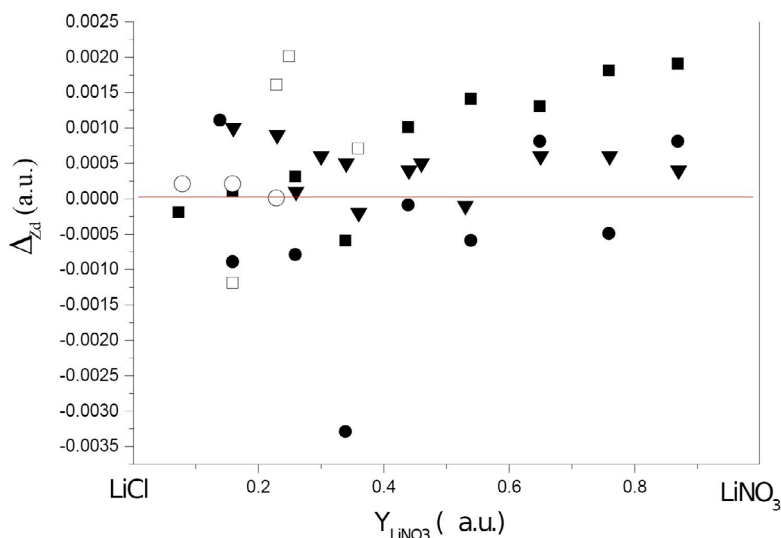**Fig. 4.**   Deviations from Zdanovskii's rule in the LiCl – LiNO$_3$ – H_2O system at 25 °C: $Y_{LiNO_3} = m_{LiNO_3} / (m_{LiNO_3} + m_{LiCl})$; $\Delta_{Zd} = 1 - m_{LiNO_3} / m_{LiNO_3}^0 - m_{LiCl} / m_{LiCl}^0$. Designations: solid squares – ln a_W = –0.6999; solid circles – ln a_W = –1.0674; up triangles – ln a_W = –1.3490; down triangles – ln a_W = –1.5055; rhombi – ln a_W = –1.6741; open squares – ln a_W = –1.8461; open circles – ln a_W = –1.9976

systems. The values of ln SP are calculated based on the solubility in the binary systems.

4. Ternary systems with two volatile components (HCl – KCl – H_2O, HCl – NaCl – H_2O) at 25 °C

The ternary systems with two volatile components considered in our study were HCl – KCl – H_2O and HCl – NaCl – H_2O at 25 °C. The existing literature presents a lot of experimental data regarding these systems [19–23]. The process of plotting of solubility diagrams (in our case, univariant crystallization curves of NaCl and KCl) is quite clear.

4.1. An algorithm for the calculation of solubility diagrams

A1) Define a_W.

A2) Find m_1^0, m_2^0 in the binary subsystems corresponding to a_W. This can be done based on the experimental data or an accurate thermodynamic model, for instance the Pitzer model. Values m_1^0, m_2^0 can correspond to both stable homogeneous solutions and supersaturated solutions. In the latter case, it is necessary to extrapolate the model for supersaturated solutions.

A3) Determine the activity of salt components in binary solutions – a_1^0, a_2^0 based on the experimental data or a thermodynamic model.

A4) Determine the thermodynamic potential of the solid phase $M_{v_{M1}} X_{v_X}$ based on the solubility of the salt – m_1^s:

$$\ln SP\left(M_{v_{M1}} X_{v_X}\right) = \ln a_1^s = v_{M1} \ln\left(v_{M1} m_1^s\right) + \\ + v_X \ln\left(v_X m_1^s\right) + \left(v_{M1} + v_X\right)\ln \gamma_1^s, \qquad (15.1)$$

where a_1^s and γ_1^s are the activity and activity coefficient of $M_{v_{M1}} X_{v_X}$ in the saturated solution.

A5) Use equation (12.3), taking into account that $a_i^{(mult)} \equiv a_i^s$:

$$\ln Z_1 = \ln SP\left(M_{v_{M1}} X_{v_X}\right) - \ln a_1^0 \qquad (15.2)$$

and find Z_1 and $Z_2 = 1 - Z_1$.

A6) Find a point on the crystallization curve $M_{v_{M1}} X_{v_X}$:

$$\ln m_i = \ln Z_i + \ln m_i^0 \quad \left(i = 1, 2\right). \qquad (15.3)$$

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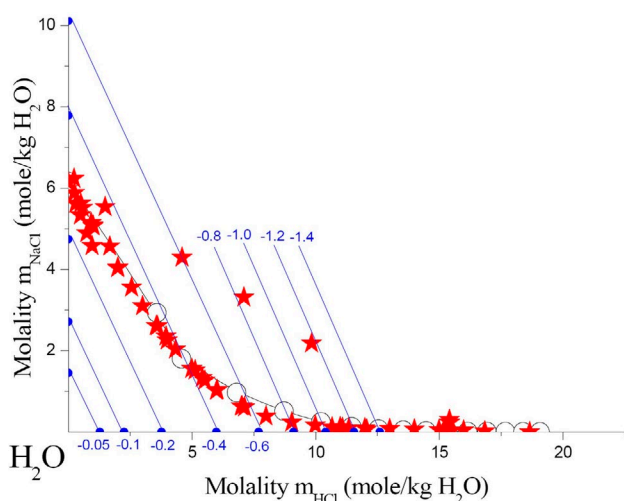
Fig. 5.1. Solubility diagram of the NaCl – HCl – H_2O system at 25 °C (open circles and lines – calculation results, red stars – experimental data [19, 20], blue lines – calculated water isoactivates, $\ln a_W$ values are shown in blue

Fig. 5.2. Solubility diagram of the KCl – HCl – H_2O system at 25 °C (open circles and lines – calculation results, red stars – experimental data [19, 23, 24], blue lines – calculated water isoactivates, $\ln a_W$ values are shown in blue

The results of the calculation are presented in Fig. 5.1 and 5.2. The figures also demonstrate the isoactivates of water calculated based on Zdanovskii's rule and extrapolated to the region of metastable supersaturated solutions. Fig. 5 demonstrates that the experimental data is in good agreement with the results of the calculation based on the binary subsystems.

4.2. An algorithm for the calculation of solid-vapor-liquid equilibrium diagrams

Let's calculate the partial pressures of volatile components, i.e. the solvent (*W*) and HCl, above saturated solutions in both systems using the following algorithm.

B1) Define a_W and calculate $\ln P_W = \ln a_W + \ln P_W^{(0)}$.

B2) Calculate $\ln a_{HCl}^0$, Z_{HCl} (see algorithm 4.1) and $P_{HCl} = a_{HCl}^0 Z_{HCl} K_{H,HCl}^m$.

B3) Calculate the total pressure of volatile components in the system: $P_{sum} = P_W + P_{HCl}$.

B4) The composition of the solution is still described by the equation (15.3):

$$\ln m_{HCl} = \ln Z_{HCl} + \ln m_{HCl}^0 ;$$
$$\ln m_{NaCl} = \ln Z_{NaCl} + \ln m_{NaCl}^0 . \tag{16}$$

The calculated pressures above saturated solutions in both systems are given in Fig. 6.1, 6.2 and Tables 5.1, 5.2. The figures demonstrate that in both systems a pseudo-azeotrope negative with regard to P_T is implemented with a minimum total
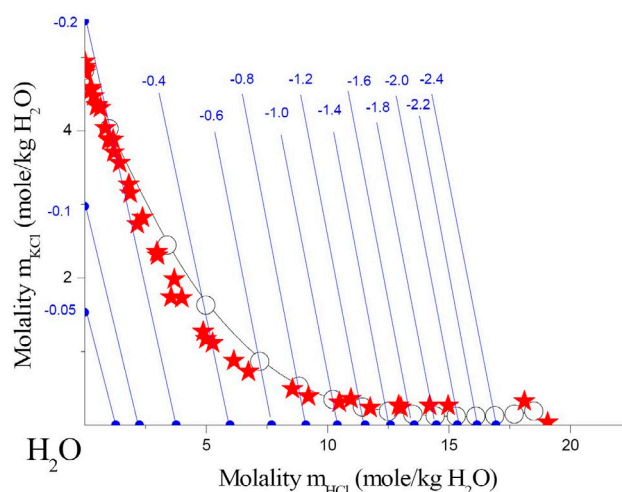
pressure – P_{Azi}. The calculation based on the binary subsystems of the ternary HCl – KCl – H_2O system at 25 °C are in good agreement with the only experimental data that we managed to find [24].

4.3. An algorithm for the calculation of vapor-liquid equilibrium diagrams in unsaturated solutions

C1) Obtain linear water isoactivates with $P_W = const$, using trivial methods (see Fig. 5.1, 5.2), including in the metastable region of supersaturated solutions.

C2) Curvilinear isoactivates or isobars of partial pressures $P_{HCl} = const$ are obtained by solving equations of the following type: $a_{HCl}^0 Z_{HCl} K_{H,HCl}^m = const$ with various a_W, finding Z_{HCl} and the corresponding compositions of solutions (m_{HCl}, m_{KCl}), followed by combining the solutions to the equations in a continuous smooth curve.

C3) The curvilinear isobars of the total pressures of volatile components $P_{sum} = const$ are also obtained by solving equations of type $a_{HCl}^0 Z_{HCl} K_{H,HCl}^m + P_W = const$ with various a_W and finding the corresponding Z_{HCl} and the corresponding compositions of solutions (m_{HCl}, m_{KCl}), followed by combining the solutions to the equations in a continuous smooth curve. The latter curves, i.e. isobars of the total pressure in both ternary systems, are given in Fig 7.1 and 7.2. In both figures, some of the vapor-liquid
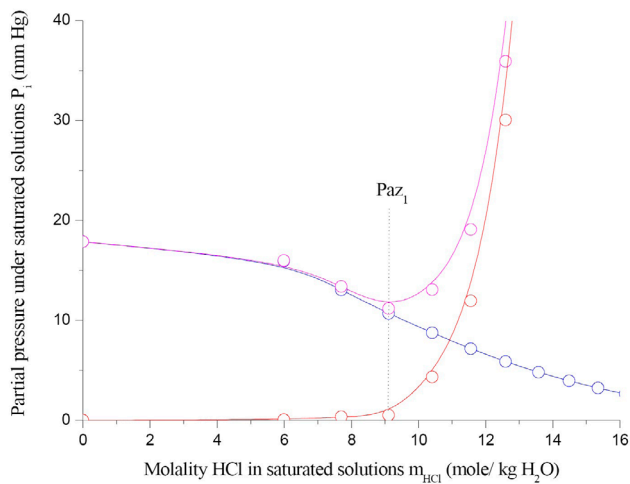
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Fig. 6.1. Dependence of partial pressures P_{H_2O} (blue lines and circles), P_{HCl} (red lines and circles), and the total pressure P_{sum} (violet lines and circles) in the NaCl – HCl – H$_2$O system at 25 °C – calculation based on binary subsystems
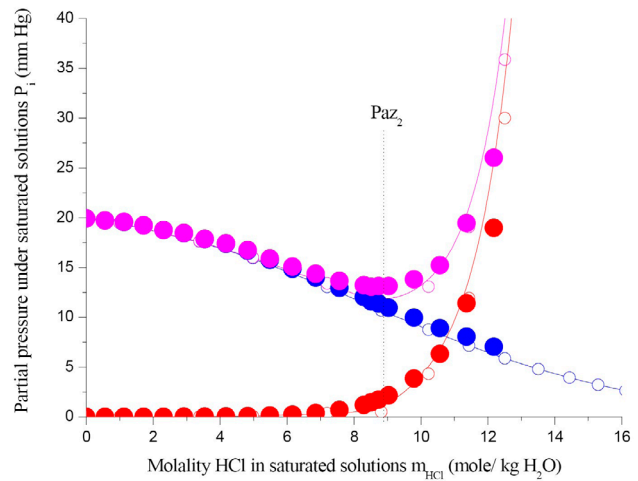

Fig. 6.2. Dependence of partial pressures P_{H_2O} (blue lines and circles), P_{HCl} (red lines and circles), and the total pressure P_{sum} (violet lines and circles) in the KCl – HCl – H$_2$O system at 25 °C – calculation based on binary subsystems, solid circles – experimental data [24]

Table 5.1 Solubility, partial, and total pressures in saturated solutions in the HCl – NaCl – H$_2$O system at 25 °C

$\ln a_W$	m^0_{HCl}	m^0_{NaCl}	$\ln a^0_{HCl}$	$\ln a^0_{NaCl}$	Z_{NaCl}	Z_{HCl}	m_{NaCl}	m_{HCl}
r.u.	mol/kg H$_2$O		r.u.		r.u.		mol/kg H$_2$O	
0.00	0.00	0.00	–	3.65	1.00	0.00	6.16	0.00
−0.05	1.28	1.45	0.19	−0.10	–	–	–	–
−0.1	2.26	2.71	1.78	1.27	–	–	–	–
−0.2	3.77	4.74	3.64	2.78	–	–	–	–
−0.4	5.99	7.78	5.93	4.56	0.4025	0.597	3.131	3.57
−0.6	7.70	10.11	7.55	5.80	0.1164	0.883	1.177	6.80
−0.8	9.11	12.05	7.87	6.81	0.0424	0.957	0.511	8.72
−1.0	10.41	13.74	10.00	7.67	0.0179	0.982	0.246	10.22
−1.2	11.56	15.24	11.01	8.43	0.0084	0.991	0.127	11.46
−1.4	12.60	16.50	11.93	9.13	0.0041	0.995	0.068	12.54
−1.6	13.58	17.85	12.78	9.78	0.0022	0.997	0.038	13.55
−1.8	14.49	19,01	13.57	10,38	0.0012	0.998	0.022	14.47
−2.0	15.35	20,09	14.32	10,95	$6.75 \cdot 10^{-4}$	0.999	0.013	15.33
−2.2	16.16	21,11	15.02	11,48	$3.97 \cdot 10^{-4}$	0.9996	0.0083	16.15

$\ln a_W$	P_W	P_{HCl}	P_{sum}
r.u.	mm Hg		
−0.2850	17.86	0.000	17.86
−0.4	15.92	0.044	15.97
.6	13.03	0.333	13.37
−0.8	10.67	0.498	11.17
−1.0	8.74	4.30	13.04
−1.2	7.15	11.92	19.08
−1.4	5.85	30.04	35.90
−1.6	4.79	70.44	75.23
−1.8	3.92	155.3	159.2
−2.0	3.21	329.2	332.4
−2.2	2.63	663.4	666.0

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Table 5.2. Solubility, partial, and total pressures in saturated solutions in the HCl – KCl – H_2O system at 25 °C

$\ln a_W$ r.u.	m_{HCl}^0	m_{KCl}^0	$\ln a_{HCl}^0$	$\ln a_{KCl}^0$	Z_{KCl}	Z_{HCl}	m_{KCl}	n_{HCl}
	mol/kg H_2O		r.u.		r.u.		mol/kg H_2O	
0.00	0.00	0.00	0.00	2.08	1.000	0.000	4.82	0.00
−0.05	1.28	1.53	0.19	−0.23	–	–	–	–
−0.1	2.26	2.97	1.78	1.04	–	–	–	–
−0.2	3.77	5.49	3.64	2.39	0.733	0.266	4,02	1.00
−0.3	4.97	7.72	4.91	3.23	0.316	0.683	2,44	3.39
−0.4	5.99	9.75	5.93	3.87	0.166	0.833	1.62	4.98
−0.6	7.70	13.49	7.55	4.83	0.063	0.936	0.86	7.20
−0.8	9.11	16.97	7.87	5.56	0.030	0.969	0.52	8.82
−1.0	10.41	20.38	10.00	6.16	0.016	0.983	0.34	10.23
−1.2	11.56	23.83	11.01	6.67	0.010	0.989	0.24	11.44
−1.4	12.60	27.48	11.93	7.10	0.0066	0.993	0.18	12.51
−1.6	13.58	31.57	12.78	7.47	0.0045	0.995	0.14	13.51
−1.8	14.49	36.85	13.57	7.80	0.0032	0.996	0.12	14.44
−2.0	15.35	41.83	14.31	7.96	0.0027	0.997	0.12	15.30
−2.2	16.16	47.43	15.02	8.09	0.0024	0.997	0.12	16.12

$\ln a_W$ r.u.	P_W	P_{HCl}	P_{sum}
	mm Hg		
−0.1720	19.90	0.00000	19.90
−0.2	19.45	0.00202	19.45
−0.3	17.60	0.0184	17.62
−0.4	15.92	0.0625	15.98
−0.6	13.03	0.354	13.39
−0.8	10.67	0.504	11.18
−1.0	8.74	4.308	13.04
−1.2	7.15	11.90	19.05
−1.4	5.85	29.98	35.84
−1.6	4.79	70.30	75.09
−1.8	3.92	155.0	158.9
−2.0	3.21	325.3	328.5
−2.2	2.63	661.6	664.3

diagrams correspond to stable solutions, and some (with high salt concentrations) correspond to metastable solutions supersaturated with respect to salts. Both figures demonstrate a univariant line of local extrema of function P_{sum} (in our case, local minimums), i.e. a negative fold on the surface of $P_{sum}(m_{HCl}, m_{salt})$ [7, 25, 26]. This fold lies between the binary azeotrope – Az_1 and the salt-water binary subsystem, where it degrades, because in binary systems dependence $P_{sum}(m_{salt})$ is strictly monotonous $\frac{dP_{sum}}{dm_{salt}} < 0$ and cannot have extrema, according to the criteria of diffusion resistance: [7–9].

5. Quaternary systems with two volatile components (HCl – NaCl – KCl – H_2O) at 25 °C

The calculation of phase equilibria in quaternary systems with two volatile components was performed using the HCl(1) – NaCl(2) – KCl(3) – H_2O) system at 25 °C.

5.1. An algorithm for the calculation of solubility diagrams

D1) Define value a_W.
D2) Find m_1^0, m_2^0, m_3^0 in the binary subsystems corresponding to a_W. This can be done based on the experimental data or an accurate thermodynamic
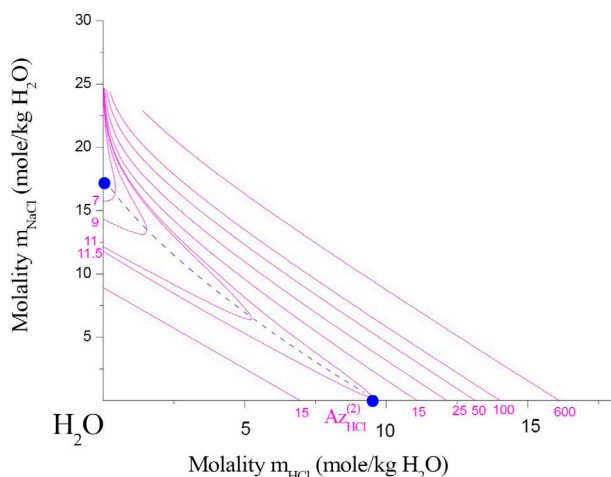
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Fig. 7.1. Dependence of the total pressure of volatile components in the NaCl – HCl – H_2O system at 25 °C: solid violet lines – calculation based on binary subsystems; P_{sum} values are represented by digits of the same color. The dotted blue line is the line of local extrema of the P_{sum} function (in our case, local minima), i.e. a negative fold on the surface of $P_{sum}(m_{HCl}, m_{NaCl})$ [7, 8]. The blue dots of the binary azeotrope in the HCl – H_2O subsystem are below and the point of degeneration of the fold is on the left

Fig. 7.2. Dependence of the total pressure of volatile components in the KCl – HCl – H_2O system at 25 °C: solid violet lines – calculation based on binary subsystems; P_{sum} values are represented by digits of the same color. The dotted blue line is the line of local extrema of the P_{sum} function (in our case, local minima), i.e. a negative fold on the surface of P_{sum} (m_{HCl}, m_{KCl}) [7, 8]. The blue dots of the binary azeotrope in the HCl – H_2O subsystem are below and the point of degeneration of the fold is on the left

model for instance the Pitzer model. Values m_1^0, m_2^0, m_3^0 can correspond to both stable homogeneous solutions and supersaturated solutions. In the latter case, it is necessary to extrapolate the model for supersaturated solutions.

D3) Determine the activity of salt components in binary solutions – a_1^0, a_2^0, a_3^0 based on the experimental data or a thermodynamic model.

D4) Determine the thermodynamic potentials of two solid phases $i = 2, 3$ (NaCl, KCl) crystallized on a single crystallization curve on the solubility diagram of the quaternary system based on the solubility of the salts – $m_i^s : \ln SP_i$.

D5) Use equation (12.3), taking into account that $a_i^{(mult)} \equiv a_i^s$:

$$\ln Z_i = \ln SP_i - \ln a_i^0 \qquad (17.1)$$

and find Z_i (i = 2, 3) and $Z_1 = 1 - Z_2 - Z_3$.

D6) Find a point on the univariant crystallization curve of phases 2 and 3:

$$\ln m_i = \ln Z_i + \ln m_i^0 \quad (i = 1, 2, 3). \qquad (17.2)$$

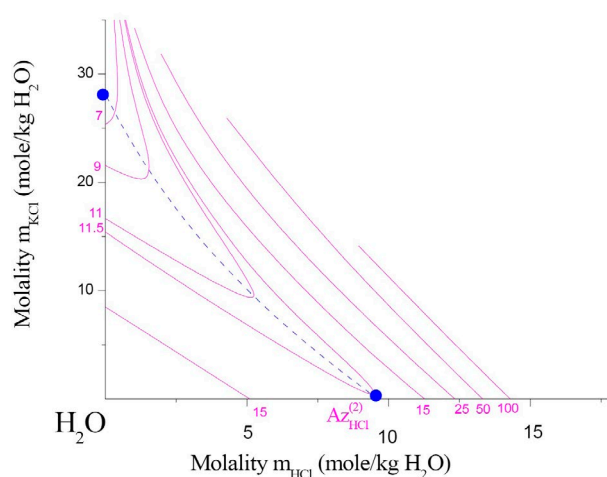The results of the calculation of the solubility diagram of the quaternary system are given in

Fig. 8.1 and Table 6. The results are presented in comparison with the experimental data provided in [24], which are in good agreement.

5.2. An algorithm for the calculation of solid$_1$-solid$_2$-liquid-vapor equilibrium diagrams

Let's calculate the partial pressures of volatile components, i.e. the solvent (*W*) and HCl, above saturated solutions in the HCl – NaCl – KCl – H_2O system at 25 °C. The following algorithm can be used.

E1) Define a_W and calculate $\ln P_W = \ln a_W + \ln P_W^{(0)}$.

E2) Calculate $\ln a_{HCl}^0$, Z_{HCl} (see algorithm 5.1) and $P_{HCl} = a_{HCl}^0 Z_{HCl} K_{H,HCl}^m$.

E3) Calculate the total pressure of volatile components in the system: $P_{sum} = P_W + P_{HCl}$.

E4) The composition of the solution is still described by the equation (17.2):

The calculated pressures above saturated solutions in both systems are given in Fig. 8.2 and Table 6. Fig. 8.2 demonstrates that a pseudo-azeotrope negative with respect to P_T is implemented with a minimum total pressure – P_{Az3}.
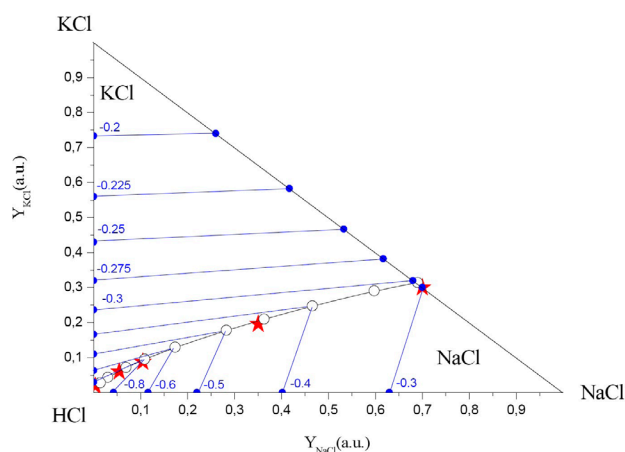
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Fig. 8.1. Solubility diagram of the KCl – NaCl – HCl – H_2O system at 25 °C (open circles and lines – calculation results, red stars – experimental data [38], blue lines – calculated water isoactivates, $\ln a_W$ values are shown in blue
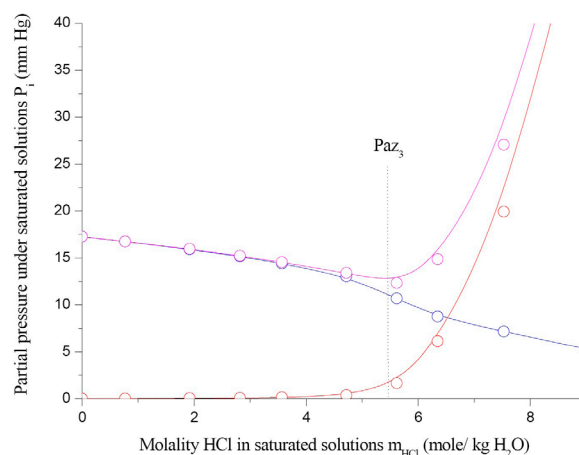

Fig. 8.2. Dependence of partial pressures P_{H_2O} (blue lines and circles), P_{HCl} (red lines and circles), and the total pressure P_{sum} (violet lines and circles) in the KCl – NaCl – HCl – H_2O system at 25 °C – calculation based on binary subsystems

Table 6. Solubility, partial, and total pressures in saturated solutions in the NaCl – KCl – HCl – H_2O system at 25 °C

$\ln a_W$ r.u.	m^0_{NaCl}	m^0_{KCl}	m^0_{HCl}	$\ln a^0_{NaCl}$	$\ln a^0_{KCl}$	Z_{NaCl}	Z_{KCl}	Z_{HCl}	m_{NaCl}	m_{KCl}	m_{HCl}
	mol/kg H_2O			r.u.						mol/kg H_2O	
−0.32	6.69	8.14	5.18	3.94	3.37	0.728	0.272	0.000	5.00	2.28	0,00
−0.35	7.11	8.76	5.49	4.19	3.57	0.582	0.229	0.187	414	2.01	0.77
−0.40	7.78	9.75	5.99	4.56	3.87	0.402	0.170	0.427	3.13	1.66	1.92
−0.45	8.41	10.72	6.45	4.90	4.14	0.286	0.130	0.583	2.40	1.39	2.82
−0.50	9.01	11.66	6.89	5.22	4.39	0.208	0.101	0.690	1.87	1.18	3.57
−0.60	10.12	13.48	7.70	5.80	4.83	0.116	0.065	0.818	1.17	0.87	4.72
−0.80	11.12	15.24	9.14	6.32	5.22	0.069	0.044	0.886	0.77	0.67	5.62
−1.00	12.05	16.97	10.41	6.81	5.56	0.042	0.031	0.926	0.51	0.53	6.35
−1.20	13.74	20.37	11.55	7.67	6.16	0.017	0.017	0.964	0.24	0.35	7.53

$\ln a_W$ r.u.	P_W	P_{HCl}	P_{sum}
	mm Hg		
−0.32	17.25	0.000	17.25
−0.35	16.74	0.0090	16.75
−0.40	15.92	0.033	15.96
−0.45	15.15	0.073	15.22
−0.50	14.41	0.134	14.54
−0.60	13.03	0.359	13.39
−0.80	10.66	1.64	12.31
−1.00	8.74	6.11	14.85
−1.20	7.15	19.90	27.06

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6. Topological isomorphism of *n*-phase equilibrium diagrams of *n*-component systems with two volatile components in decreased concentration spaces

This section focuses on the topological isomorphism of equilibrium diagrams of multicomponent multiphase systems containing two volatile components in univariant multicomponent multiphase systems. Earlier studies considered some particular systems of the same or similar types (for instance, [27]).

6.1. Topological isomorphism of three-phase equilibrium diagrams of ternary systems with two volatile components

Let's consider a three-phase equilibrium (solid phase – non-volatile component 3 (*s*) – vapor, consisting of two volatile components 1 – volatile acid 2 – solvent (*v*) – liquid solution, consisting of all the three components of the ternary system) at a constant temperature T = const. For instance, let's consider the following system: HCl(1) – H_2O(2) – NaCl(3). Let's introduce the partial Gibbs energy:

$$G^{[3]} = G - \mu_3 n_3 = \sum_{i=1}^{2} \mu_i n_i, \tag{18}$$

where μ_i and n_i are the chemical potential and the number of moles of the *i*-th volatile component.

Let's consider a heterogeneous ternary system and introduce a scalar quantity $y_1^{(i)}$, where $y_1^{(i)}$ is the mole fraction of the 1st component (in the *i*-th phase) in the concentration space reduced with respect to the 3rd component. These are the so-called Janecke indices:

$$y_1 = n_1 / \sum_{j=1}^{2} n_j. \tag{19}$$

The independent characteristic parameters of the partial molar Gibbs energy (18) are as follows: temperature – T, pressure – P, the Janecke index – y_1, and the chemical potential of the 3rd component in the solid phase – μ_3. The equation of the two-phase $(\alpha-\beta)$ equilibrium shift can be described by the following system of generalized differential van der Waals equations:

$$(y_1^{(\alpha)} - y_1^{(\beta)})G_{11}^{[3](\alpha)}dy_1^{(\alpha)} = \\ = S^{[3](\alpha\to\beta)}dT - V^{[3](\alpha\to\beta)}dP + n_3^{[3](\alpha\to\beta)}d\mu_3, \tag{20}$$

$$(y_1^{(\beta)} - y_1^{(\alpha)})G_{11}^{[3](\beta)}dy_1^{(\beta)} = \\ = S^{[3](\beta\to\alpha)}dT - V^{[3](\beta\to\alpha)}dP + n_3^{[3](\beta\to\alpha)}d\mu_3, \tag{21}$$

where:

$$S^{[3](\alpha\to\beta)} = \left[S^{[3](\beta)} - S^{[w](\alpha)} + (y_1^{(\beta)} - y_1^{(\alpha)})\nabla S^{[3](\alpha)} \right]$$
$$S^{[3](\beta\to\alpha)} = \left[S^{[3](\alpha)} - S^{[3](\beta)} + (y_1^{(\alpha)} - y_1^{(\beta)})\nabla S^{[3](\beta)} \right]$$
$$V^{[3](\alpha\to\beta)} = \left[V^{[3](\beta)} - V^{[3](\alpha)} + (y_1^{(\beta)} - y_1^{(\alpha)})\nabla V^{[3](\alpha)} \right]$$
$$V^{[3](\beta\to\alpha)} = \left[V^{[3](\alpha)} - V^{[3](\beta)} + (y_1^{(\alpha)} - y_1^{(\beta)})\nabla V^{[3](\beta)} \right] \tag{22}$$
$$n_w^{[3](\alpha\to\beta)} = \left[n_w^{[3](\beta)} - n_w^{[3](\alpha)} + (y_1^{(\beta)} - y_1^{(\alpha)})\nabla n_3^{(3)(\alpha)} \right]$$
$$n_w^{[3](\beta\to\alpha)} = \left[n_w^{[3](\alpha)} - n_w^{[3](\beta)} + (y_1^{(\alpha)} - y_1^{(\beta)})\nabla n_W^{(3)(\beta)} \right],$$

where $V^{[3](\tau)}$, $S^{[3](\tau)}$ and $n_w^{[3](\tau)}$ are the molar volume, entropies, and numbers of moles of the 3rd component of phase τ, calculated without taking into account the number of moles of the salt (per 1 mole of volatile components). The $\nabla V^{[3](\tau)}$, $\nabla S^{[3](\tau)}$, $\nabla n_w^{[3](\tau)}$ functions are gradients of concentration of the corresponding functions in the reduced concentration space, $\left(\partial V^{[3](\tau)} / \partial y_1^{(\tau)}\right)_{T,P,\mu_3^{(\tau)}}$, $\left(\partial S^{[3](\tau)} / \partial y_1^{(\tau)}\right)_{T,P,\mu_3^{(\tau)}}$, and $\left(n_w^{[3](\tau)} / \partial y_1^{(\tau)}\right)_{T,P,\mu_3^{(\tau)}}$, respectively; $y_1^{(\tau)}$ is the parameter, characterizing the state of the figurative point of phase τ in the reduced concentration space; $dy_1^{(\tau)}$ characterizes the displacement of $y_1^{(\tau)}$ according to the displacement of the two-phase equilibrium; $G_{11}^{[3](\tau)}$ is determined as:

$$G_{11}^{[3](\alpha)} = \left(\frac{\partial^2 G^{[1](\alpha)}}{\partial y_1^{(\alpha)2}} \right)_{T,P,\mu_3^{(\alpha)}} \tag{23}$$

and

$$G_{11}^{[3](\beta)} = \left(\frac{\partial^2 G^{[1](\beta)}}{\partial y_1^{(\beta)2}} \right)_{T,P,\mu_3^{(\beta)}}. \tag{24}$$

According to the diffusion resistance criteria and Sylvester's criterion, for the positive definite quadric forms, the following is true:

$$G_{11}^{[3](\tau)} > 0. \tag{25}$$

The $S^{[3](\alpha\to\beta)}, S^{[3](\beta\to\alpha)}, V^{[3](\alpha\to\beta)}, V^{[3](\beta\to\alpha)}, n_w^{[3](\beta\to\alpha)}$ parameters have the physical senses of entropy, the volume and the number of moles of the 3rd

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component in the isotherm–isobar–isopotential (with respect to the 3rd component) process of formation of one mole of phase β from an infinitely large.

Let's assume that the α phase is a liquid solution (l), the β phase is vapor (v), and the α → β equilibrium is (l)–(v), $dT = 0$, $d\mu_3 = 0$. The latter is true because the standard chemical potential of the solid phase (s), μ_3, depends on the temperature only. Therefore, we are dealing with a three-phase equilibrium (l)–(v)–(s). Let's rewrite the system of differential equations (20, 21):

$$(y_1^{(l)} - y_1^{(v)})G_{11}^{[3](l)}dy_1^{(l)} = -V^{[3](l \to v)}dP \qquad (26)$$

$$(y_1^{(v)} - y_1^{(l)})G_{11}^{[3](v)}dy_1^{(v)} = -V^{[3](v \to l)}dP \ . \qquad (27)$$

Naturally, the equation cannot be used with $dP = 0$, $dT \neq 0$, because then $d\mu_3 \neq 0$, and the corresponding term should be added to equations (26, 27).

Based on the physical sense, $V^{[3](l \to v)} > 0$, $V^{[3](v \to l)} < 0$, and therefore we can formulate three analogues of the three Gibbs–Konovalov and Gibbs–Roozeboom rules.

First rule.

When moving along the crystallization curve of the non-volatile component on the isothermal solubility diagram of a ternary system, the total pressure of vapors above saturated solutions increases (decreases) following an increase in the Janecke index of the volatile component (excluding the non-volatile component), whose concentration in the ternary system of vapor is larger (smaller) than in the solution:

$$\left[dP / dy_1^{(l)} \right]_{T,\mu_3^{(\tau)}} > (<)0 \ , \ \text{if} \ y_1^{(v)} > (<)y_1^{(l)} \ . \qquad (28.1)$$

Second rule.

When moving along the crystallization curve of the non-volatile component on the isothermal solubility diagram of a ternary system in a reduced (excluding the non-volatile component) concentration space, the total pressure of the volatile components passes through the extremum, if the compositions of the existing phases in the reduced concentration space, i.e. the Janecke indices, coincide. These points will be called pseudo-azeotropes - P_{Az}.

$$\left[dP / dy_1^{(l)} \right]_{T,\mu_3^{(\tau)}} = 0, \ \text{if} \ y_1^{(v)} = y_1^{(l)} \ . \qquad (28.2)$$

Third rule.

Dividing equation (26) by equation (27) we obtain:

$$\left[dy_1^{(l)} / dy_1^{(v)} \right]_{T,\mu_3^{(\tau)}} =$$
$$= -\left[G_{11}^{[3](v)} / G_{11}^{[3](v)} \right]\left[V^{[3](l \to v)} / V^{[3](v \to l)} \right] > 0. \qquad (28.3)$$

When moving along the crystallization curve of the non-volatile component on the isothermal solubility diagram of a ternary system in a reduced (excluding the non-volatile component) concentration space, the Janecke indices of the equilibrium liquid and vapor phases change simbatically.

6.2. Topological isomorphism of four-phase equilibrium diagrams of four-component systems with two volatile components

Let's consider a four-phase equilibrium (solid non-volatile component 3 (s_1) – solid non-volatile component 4 (s_2) – vapor, consisting of two volatile components 1 – volatile acid 2 and solvent (v) – liquid solution, consisting of all the four components of the four-component system) at a constant temperature $T = $ const. For instance, let's consider the following system: HCl(1) – H$_2$O(2) – NaCl(3) – KCl(4). Let's introduce the partial Gibbs energy:

$$G^{[3,4]} = G - \mu_3 n_3 - \mu_4 n_4 = \sum_{i=1}^{2}\mu_i n_i \ . \qquad (29)$$

Let's consider a heterogeneous four-component system and introduce a scalar quantity in the twice reduced concentration space $y_1^{(i)}$, where $y_1^{(i)}$ is the molar fraction of the 1-st component (in the i-th phase) in the twice reduced concentration space (excluding components 3 and 4). In this case, the Janecke indices are set by the following relation:

$$y_1 = n_1 \left/ \sum_{j=1}^{2}n_j \right. \ . \qquad (30)$$

The characteristic parameters of the partial molar Gibbs energy (29) are the following: temperature – T, pressure – P, the Janecke index – y_1, and the chemical potentials of salts – μ_3, μ_4. The equation of the two-phase (α–β) equilibrium shift can be described by the following system of differential van der Waals equations:

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$$(y_1^{(\alpha)} - y_1^{(\beta)})G_{11}^{[3,4](\alpha)}dy_1^{(\alpha)} = S^{[3,4](\alpha\to\beta)}dT - $$
$$-V^{[3,4](\alpha\to\beta)}dP + n_3^{[3,4](\alpha\to\beta)}d\mu_3 + n_4^{[3,4](\alpha\to\beta)}d\mu_4, \quad (31)$$

$$(y_1^{(\beta)} - y_1^{(\alpha)})G_{11}^{[3,4](\beta)}dy_1^{(\beta)} = S^{[3,4](\beta\to\alpha)}dT - $$
$$-V^{[3,4](\beta\to\alpha)}dP + n_3^{[3,4](\beta\to\alpha)}d\mu_3 + n_4^{[3,4](\beta\to\alpha)}d\mu_4, \quad (32)$$

where parameters $G_{11}^{[3,4](\tau)}$, $S^{[3,4](\alpha\to\beta)}$, $S^{[3,4](\beta\to\alpha)}$, $V^{[3,4](\alpha\to\beta)}$, $V^{[3,4](\beta\to\alpha)}$, $n_3^{[3,4](\alpha\to\beta)}$, $n_4^{[3,4](\alpha\to\beta)}$, $n_5^{[3,4](\beta\to\alpha)}$, and $n_4^{[3,4](\beta\to\alpha)}$ have the same sense as the parameters in equations (22) with the only addition – $\mu_4^{(\tau)}$ should be constant for the corresponding derivatives:

$$\left(\partial V^{[3](\tau)} / \partial y_1^{(\tau)}\right)_{T,P,\mu_3^{(\tau)},\mu_4^{(\tau)}}, \left(\partial S^{[3](\tau)} / \partial y_1^{(\tau)}\right)_{T,P,\mu_3^{(\tau)},\mu_4^{(\tau)}},$$

$$\left(n_w^{[3](\tau)} / \partial y_1^{(\tau)}\right)_{T,P,\mu_3^{(\tau)},\mu_4^{(\tau)}}, G_{11}^{[3](\tau)} = \left(\frac{\partial^2 G^{[1](\tau)}}{\partial y_1^{(\tau)2}}\right)_{T,P,\mu_3^{(\tau)},\mu_4^{(\tau)}}.$$

Parameters $S^{[3](\alpha\to\beta)}$, $S^{[3](\beta\to\alpha)}$, $V^{[3](\alpha\to\beta)}$, $n_w^{[3](\alpha\to\beta)}$, and $n_w^{[3](\alpha\to\beta)}$ reflect the changes in the entropy, volume, and the number of moles of the components (3, 4) during the isotherm–isobar–isopotential (with regard to the 3rd and 4th components) process of formation of one mole of phase β from an infinitely large mass of phase α, and vice versa in the concentration space, reduced with respect to the 3rd and 4th components.

Let's assume that the α phase is a liquid solution (l), the β phase is vapor (v), and the $\alpha \to \beta$ equilibrium is (l)–(v), dT = 0, $d\mu_3 = d\mu_4 = 0$. The latter is true because the standard chemical potentials of the components in the solid phase (s_1, s_2) μ_3 and μ_4 depend on the temperature only. Therefore, we are dealing with a four-phase equilibrium (l)–(v)–(s_1)–(s_2). Let's rewrite equations (31, 32) for the set conditions. Then we can easily derive equations (26, 27).

Therefore, we can formulate three analogues of the Gibbs–Konovalov and Gibbs–Roozeboom rules, which will be true for the twice reduced concentration space:

$$\left[dP / dy_1^{(l)}\right]_{T,\mu_3^{(\tau)},\mu_4^{(\tau)}} > (<)0, \text{ if } y_1^{(v)} > (<)y_1^{(l)}; \quad (33.1)$$

$$\left[dP / dy_1^{(l)}\right]_{T,\mu_3^{(\tau)},\mu_4^{(\tau)}} = 0, \text{ if } y_1^{(v)} = y_1^{(l)}; \quad (33.2)$$

$$\left[dP / dy_1^{(l)}\right]_{T,\mu_3^{(\tau)},\mu_4^{(\tau)}} =$$
$$= -\left[G_{11}^{[3](v)} / G_{11}^{[3](v)}\right]\left[V^{[3](l\to v)} / V^{[3](v\to l)}\right] > 0. \quad (33.3)$$

The wording of the analogues is the same as that of the ones presented in section 6.1, the only difference being the following: "When moving along the **co-crystallization** curve of the **two** non-volatile components on the isothermal solubility diagram of a **four-component** system in a **twice** reduced (excluding both non-volatile components) concentration space...".

6.3. Topological isomorphism of n-phase equilibrium diagrams of n-component systems with two volatile components

Naturally, the suggested analogues of the three Gibbs–Konovalov and Gibbs–Roozeboom rules can be applied to *n*-phase heterogeneous systems within *n*-component systems with two volatile components. Let's consider a phase equilibrium (solid pure non-volatile component 3 (s_1) – solid pure non-volatile component 4 (s_2) – solid pure non-volatile component *n* (s_{n-2}) – vapor, consisting of two volatile components 1 – volatile acid and 2 – solvent (*v*) – liquid solution, consisting of 1, 2, 3...*n* components) at a constant temperature *T* = const. In this case, we are dealing with an (*n*-2)-time reduced concentration space and can formulate another three analogues of the Gibbs–Konovalov and Gibbs–Roozeboom rules, which will be true for an (*n*-2)-time reduced concentration space:

$$\left[dP / dy_1^{(l)}\right]_{T,\mu_3^{(\tau)},\mu_4^{(\tau)},...,\mu_n^{(\tau)}} > (<)0, \text{ if } y_1^{(v)} > (<)y_1^{(l)}; (34.1)$$

$$\left[dP / dy_1^{(l)}\right]_{T,\mu_3^{(\tau)},\mu_4^{(\tau)},...,\mu_n^{(\tau)}} = 0, \text{ if } y_1^{(v)} = y_1^{(l)}; \quad (34.2)$$

$$\left[dP / dy_1^{(l)}\right]_{T,\mu_3^{(\tau)},\mu_4^{(\tau)},...,\mu_n^{(\tau)}} =$$
$$= -\left[G_{11}^{[3](v)} / G_{11}^{[3](v)}\right]\left[V^{[3](l\to v)} / V^{[3](v\to l)}\right] > 0. \quad (34.3)$$

The wording of the analogues is the same as that of the ones presented in section 6.1, the only difference being the following: "When moving along the **co-crystallization** curve of **(n−2)** non-volatile components on the isothermal solubility diagram of an **n-component** system in an **(n−2)-time** reduced (excluding **(n−2)** non-volatile components) concentration space...".

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6.4. Topological isomorphism of n-phase equilibrium diagrams of n-component systems with two volatile components with crystal solvates (crystalline hydrates) of solid components of constant composition

Until now, we assumed that all solid phases of constant composition that are in equilibrium with vapor and liquid solution are pure salt-type components. Let's assume that crystal solvates (crystalline hydrates) of solid solutions of constant compositions are crystallized in the system. Are they then the true analogues of the three Gibbs–Konovalov and Gibbs–Roozeboom rules presented in (34.1–34.3)? The answer to this question is positive provided that we consider crystalline hydrates or compounds of constant compositions rather than particular salts as independent components of the system. This can be done, because the independent components, or variables of the composition of a multicomponent system, are random, with only the number of independent components being constant. Therefore, the laws will be true in the concentration space reduced with respect to the new components. For instance, on the crystallization curve of crystalline hydrate LiCl·H_2O in the HCl(1) – H_2O(2) – LiCl(3) system, all the analogues of the Gibbs–Konovalov and Gibbs–Roozeboom rules are true (28.1–28.3), if we recalculate the Janecke indices for the new components of the system: HCl(1) – H_2O(2) –

LiCl·H_2O(3). In this case, the molar fractions in the new set of variables $n_i^{(new)}$ are easily calculated based on the molar fractions in the previous set of variables $n_i^{(old)}$: $n_{LiCl \cdot H_2O}^{(new)} = n_{LiCl}^{(old)}$, $n_{HCl}^{(new)} = n_{HCl}^{(old)}$, $n_{H_2O}^{(new)} = n_{H_2O}^{(old)} - n_{LiCl}^{(old)}$. Let's consider another example: for the co-crystallization curve of $MgCl_2 \cdot CaCl_2 \cdot 12H_2O$ and crystalline hydrate $MgCl_2 \cdot 6H_2O$ in the HCl(1) – H_2O(2) – $MgCl_2$(3) – $CaCl_2$(4) system the analogues of the said laws (28.1–28.3) are true, if we recalculate the molar fractions of the components with respect to HCl(1) – H_2O(2) – $MgCl_2 \cdot 6H_2O$(3) – $MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(4). The recalculation is performed based on the relations:
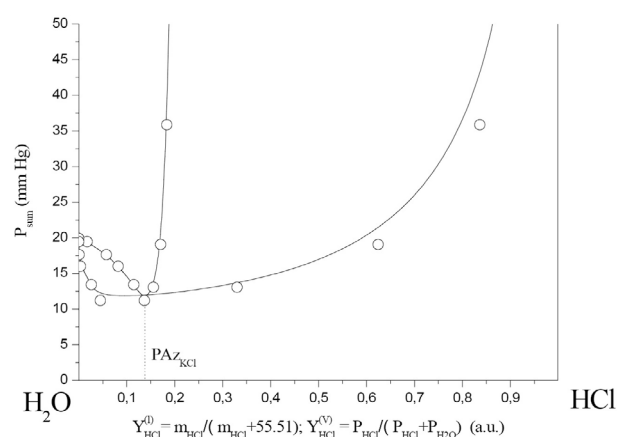

Fig. 9.2. Liquid-vapor phase diagram in the KCl – HCl – H_2O system at 25 °C in variables: the total vapor pressure of volatile components is the Yanecke HCl index; P_{AzKCl} is a pseudo-azeotrope when moving along the NaCl crystallization curve
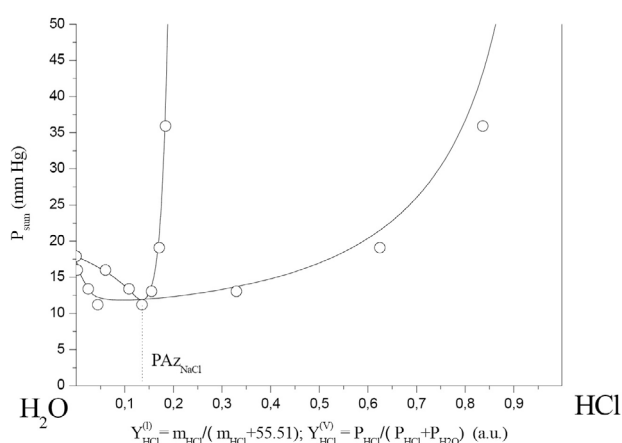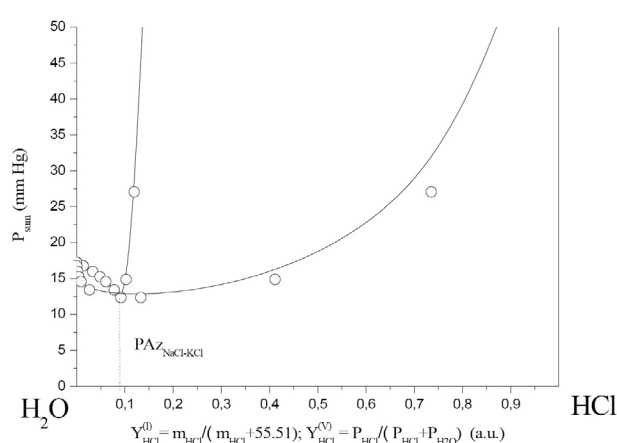

Fig. 9.1. Liquid-vapor phase diagram in the NaCl – HCl – H_2O system at 25 °C in variables: the total vapor pressure of volatile components is the Yanecke HCl index; P_{AzNaCl} is a pseudo-azeotrope when moving along the NaCl crystallization curve

Fig. 9.3. Liquid-vapor phase diagram in the KCl – NaCl – HCl – H_2O system at 25 °C in variables: the total vapor pressure of volatile components is the Yanecke HCl index; $P_{AzNaCl-KCl}$ is a pseudo-azeotrope when moving along the KCl and NaCl co-crystallization branch

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$$n^{(new)}_{\mathrm{MgCl_2 \cdot CaCl_2 \cdot 12H_2O}} = n^{(old)}_{\mathrm{CaCl_2}}, \qquad n^{(new)}_{\mathrm{MgCl_2 \cdot 6H_2O}} = n^{(old)}_{\mathrm{MgCl_2}} - n^{(old)}_{\mathrm{CaCl_2}},$$

$$n^{(new)}_{\mathrm{HCl}} = n^{(old)}_{\mathrm{HCl}}, \qquad n^{(new)}_{\mathrm{H_2O}} = n^{(old)}_{\mathrm{H_2O}} - 6\left[n^{(old)}_{\mathrm{MgCl_2}} + n^{(old)}_{\mathrm{CaCl_2}} \right] -$$

$$- 12 n^{(old)}_{\mathrm{CaCl_2}}.$$

6.5. Application of the suggested analogues of the Gibbs–Konovalov and Gibbs–Roozeboom rules to ternary and quaternary systems

Fig. 9.1–9.3 demonstrate some examples of the suggested analogues of the Gibbs–Konovalov and Gibbs–Roozeboom rules implemented for univariant curves of three-phase equilibrium in ternary systems (HCl – H$_2$O – NaCl and HCl – H$_2$O – KCl at 25 °C) and a quaternary system (HCl – H$_2$O – NaCl – KCl at 25 °C). In the first case, three-phase equilibria (s–l–v) were considered, and in the second case – four-phase equilibria (s$_1$–s$_2$–l–v). In the first case, the concentration space was reduced with respect to NaCl, and in the second case it was reduced with respect to NaCl and KCl. In both cases, the variables of the composition were the Janecke indices of the volatile components of the system – Y_{HCl}, Y_W. Fig. 9.1–9.3 show that the three systems are in complete agreement with the suggested analogues of the three rules. Each system has one pseudo-azeotrope – P_{Azj} (index j corresponds to the solid phase(s) with respect to which the considered solution is saturated). P_{Azj} complies with the minimum $P_{\mathrm{sum}} = P_W + P_{\mathrm{HCl}}$. All the diagrams are also limited from above by the boiling point of the solution at $P_{\mathrm{sum}} = 760$ mm Hg.
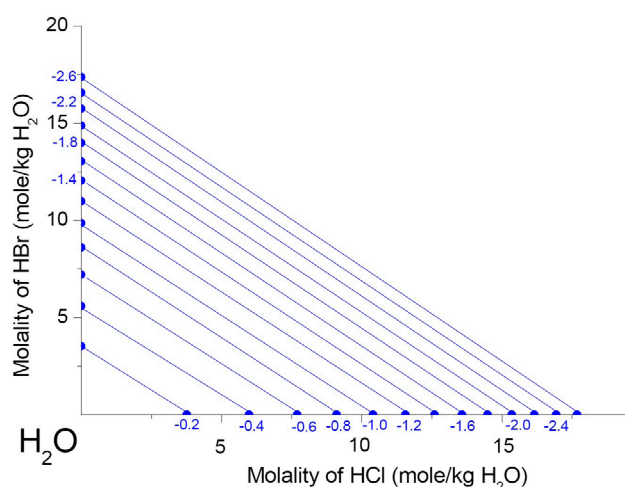

Fig. 10.1. Water isoacivates in the ternary HCl – HBr – H$_2$O system at 25 °C, ln a_W values are shown in blue

7. Ternary systems with three volatile components (HCl – HBr – H$_2$O) at 25 °C

To demonstrate the possibility of the calculation of phase diagrams of ternary systems with three volatile components, we considered the HCl – HBr – H$_2$O system at 25 °C. Solid phases cannot be formed in such systems under the defined conditions. So, naturally, there is the only type of equilibrium diagram, which we consider below.

7.1. An algorithm for the calculation of vapor-liquid equilibrium diagrams in unsaturated solutions

F1) Define a_W.

F2) Obtain linear water isoactivates with $P_W = P_W^{(0)}$ ($a_W = const$) based on the data regarding the binary subsystems (see Fig. 10.1).

F3) Curvilinear isoactivates or isobars of partial pressures $P_{\mathrm{HCl}} = const$ are obtained by solving equations of the following type: $a^0_{\mathrm{HCl}} Z_{\mathrm{HCl}} K^m_{\mathrm{H,HCl}} = const$ with various a_W, finding Z_{HCl} and the corresponding compositions of solutions (m_{HCl}, m_{KCl}) (see (13)), followed by combining the solutions to the equations in a continuous smooth curve.

F4) Curvilinear isoactivates or isobars of partial pressures $P_{\mathrm{HBr}} = const$ are obtained by solving equations of the following type:

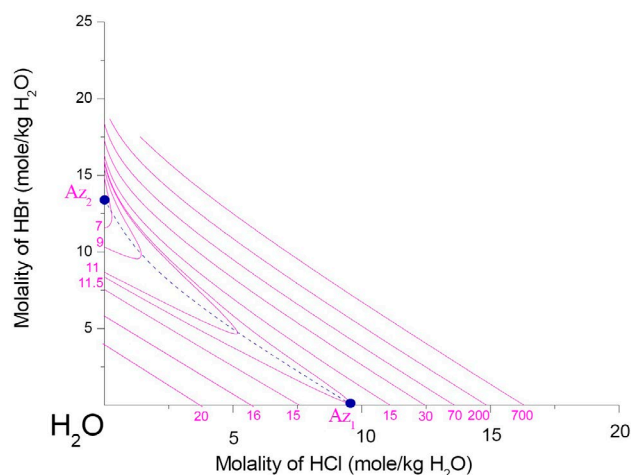**Fig. 10.2.** Lines of equal total pressures of volatile components in the ternary HCl – HBr – H$_2$O system at 25 °C, P_{sum} values in mm Hg are shown in violet. The dotted blue line is the line of local extrema of the Psum function, i.e. a negative fold on the $P_{\mathrm{sum}}(m_{\mathrm{HCl}}, m_{\mathrm{HBr}})$ surface [7, 8]; the blue dots are binary azeotropes in the subsystems HCl – H$_2$O and HBr – H$_2$O

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$a_{HBr}^0 Z_{HBr} K_{H,HBr}^m = const$ with various a_W, finding Z_{HBr} and the corresponding compositions of solutions (m_{HCl}, m_{KCl}) (see (13)).

F5) Curvilinear isobars of the total pressures of volatile components $P_{sum} = const$ are obtained by solving equations of the following type: $a_{HCl}^0 Z_{HCl} K_{H,HCl}^m + a_{HBr}^0 (1 - Z_{HCl}) K_{H,HBr}^m + P_W = const$ with various a_W, finding the corresponding Z_{HCl} and the compositions of solutions (m_{HCl}, m_{KCl}), followed by combining the solutions to the equations in a continuous smooth curve. The latter curves, i.e. isobars of the total pressure in the considered ternary system, are given in Fig 10.2. Both figures demonstrate a univariant line of local extrema of function P_{sum} (local minimums), i.e. a negative fold on the surface of $P_{sum}(m_{HCl}, m_{salt})$ [7, 26, 27]. This fold lies between the binary azeotrope Az_1 and another binary azeotrope Az_2, (see Fig. 10.2).

8. Conclusions

The article presented an algorithm for the calculation of vapor-liquid phase equilibria in multicomponent quasi-simple systems complying with Zdanovskii's rule. The algorithm is based entirely on the data regarding binary subsystems. The algorithm was tested using three- and four-component water-electrolyte systems with one, two, or three volatile components. The results of the calculations are in good agreement with the experimental data. Analogues of the Gibbs–Konovalov and Gibbs–Roozeboom rules were formulated and proved for the compositions of the solutions moving along univariant curves of n-phase equilibria in n-component systems at a constant temperature.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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