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CRITICAL STATES IN MULTICOMPONENT LIQUID-PHASE SYSTEMS WITH CHEMICAL INTERACTION OF SUBSTANCES

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INTRODUCTION

The thesis is devoted to the study of critical phenomena in multicomponent systems with chemical interaction of substances. The formulation of the problem was determined by the fact that studies of modern complex physicochemical systems have led to a number of new problems that were not the subject of study in early and traditional works in the field of the theory of critical phenomena. Of course, one can point to a number of modern achievements, for example, in the field of studying supercritical fluids and their practical application in chemical technology, including organic and inorganic synthesis, technologies of new promising materials and other areas. At the same time, studies of critical and near-critical states as a boundary region of supercritical phases remain significant, including for the development of the theory of processes in supercritical fluids. For example, in multicomponent systems, the region of critical states can no longer be a single point, but a surface and a hypersurface in thermodynamic space. Even more complex problems arise during chemical reactions in critical phases. It should be noted that the study of critical phases requires increased accuracy, due to known conditions: the critical state belongs simultaneously to the boundary of the stability regions with respect to discontinuous and continuous changes in state, in the critical phase the processes of nucleation and decay of nuclei of new phases continuously occur. Therefore, at present, the development of the theory of critical phenomena in complex multicomponent heterogeneous systems, especially in the chemical interaction of substances, is significantly hampered by the insufficiency of the experimental database. It is also possible to point out the need to search for new variants of thermodynamic description of critical phases. The existing traditional forms (the first and second equations of the critical phase) are quite complex for practical application in the case of multicomponent systems, which requires the development of new thermodynamic approaches.

In experimental terms, the main difference between the tasks set in the thesis and the existing works is also determined by the objects of study: multicomponent heterogeneous systems with chemical interaction (chemical reactions), the sets of critical states of which should be represented as two-dimensional or multidimensional regions in thermodynamic space (surfaces and hypersurfaces). New information includes data on the compositions corresponding to critical states, thermodynamic characteristics of critical regions, equilibrium parameters of fluid phases, as well as information on the topological features of critical curves and surfaces. The specified experimental information on critical surfaces in systems with chemical reactions is quite limited in the world literature. In general, based on the analysis of publications in international journals, the statement of the thesis tasks and its results have no direct analogues in the modern literature. The set of these problems should be attributed to modern and topical problems of fundamental natural scientific and practical significance. All this determines **the relevance of the thesis** in relation to the development of thermodynamic aspects of the theory of critical phenomena and experimental thermodynamic databases on critical states of multicomponent systems with chemical interaction of substances.

Thus, **the goal of the thesis** is focused on the fundamental problem of studying critical phenomena in multicomponent heterogeneous mixtures with chemical reactions, analyzing the topology of diagrams, obtaining direct experimental data on critical manifolds in thermodynamic space, and developing methods for thermodynamic analysis of critical states.

The main tasks to be solved in the thesis:

- To obtain experimental data on phase equilibria in multicomponent liquid-liquid systems (systems of four substances and constituent ternary and binary subsystems) formed by components of mixtures including reagents (reactants) and products of reactions of synthesis and hydrolysis of carboxylic acid esters.
- Obtain experimental data on chemical equilibrium in heterogeneous stratified mixtures of four substances formed by reactants and reaction products of synthesis and hydrolysis of carboxylic acid esters.
- Obtain experimental data on critical states of liquid-liquid equilibrium in systems of four substances with chemical interaction, as well as in their constituent subsystems.
- Conduct thermodynamic and topological analysis of the features of multicomponent systems with chemical interaction and critical phases, including the mutual arrangement of critical curves and surfaces, manifolds of phase and chemical equilibrium.
- Develop a new approach and obtain new forms of thermodynamic conditions of the critical state in systems with chemical reactions.

The scientific novelty of the results of the thesis is characterized by the following**:**

- A comprehensive set of experimental data on critical phases in multicomponent liquid-phase systems with chemical interaction of the substances forming them has been obtained, which has no direct analogues in the world literature.
- Analysis of the mutual arrangement of critical curves and surfaces, manifolds of phase and chemical equilibrium was carried out on the basis of the obtained experimental data, which made it possible, in most cases, to present a correct and justified characteristic (illustration) of not only combined phase and chemical equilibrium, but also topological features of critical manifolds in the case of chemical interaction in a multicomponent mixture.
- For the first time, experimental data on chemically equilibrium critical phases and the arrangement of the corresponding manifolds in thermodynamic space have been obtained.
- New forms of stability conditions and relationships determining the boundaries of stability of multicomponent phases have been proposed.
- An approach to formulating thermodynamic conditions of a critical state in the case of simultaneous phase and chemical equilibrium has been developed.

The practical significance of the results is determined by the following:

- The obtained extensive complex of data on phase and chemical equilibria in systems with reactions of synthesis/hydrolysis of carboxylic acid esters, topology of state diagrams, is directly additionally oriented towards the organization of processes of synthesis, separation and combined processes of organic synthesis technology.
- The results of the study of phase and chemical equilibria, including simultaneous equilibrium, are a significant development of thermodynamic databases on multicomponent systems with chemical interaction
- The complex of data on critical states in multicomponent mixtures with chemical interaction forms the basis of the thermodynamic database on the specified systems.

The author's personal contribution consisted of setting experimental and theoretical tasks, planning and conducting experiments, analyzing, summarizing and presenting the obtained data, preparing and writing scientific articles based on the results of the thesis. All experimental results were obtained at the Institute of Chemistry of St. Petersburg State

University, at the Department of Chemical Thermodynamics and Kinetics, as well as using the equipment of the Scientific Park of St. Petersburg State University, Resource Centers: "Methods of Analysis of the Composition of Substances", "Magnetic Resonance Research Methods", "Thermogravimetric and Calorimetric Research Methods", "Computer Center".

The studies were also supported by the Russian Foundation for Basic Research and the Russian Science Foundation. RFBR grants: No. 18-33-20138 mol_a_ved "Phase, chemical and membrane processes in biofuel systems: synthesis and separation", 2018-2020 (head), No. 13-03-00985a "Chemical and phase processes in the vicinity of the critical state of heterogeneous systems with chemical interaction" 2013-2015 (head), No. 19-03-00375 "Application of nonequilibrium thermodynamics methods to solve theoretical problems of chemical engineering: stability of multicomponent systems, phase and membrane separation, reaction-mass transfer processes", 2019-2021. (performer), No. 16-33-00129 “Development of a thermodynamic approach to the study of reaction-mass transfer processes in systems with an esterification reaction”, 2016 (performer).

RSF Grants: No. 20-73-10007 "Deep Eutectic Solvents in Biodiesel Production and Purification Processes", 2020-2023 (head), No. 20-73-10007-P "Deep Eutectic Solvents in Biodiesel Production and Purification Processes", 2023-2025 (extension, head), No. 17-73-10290 "Thermodynamics of Reaction-Mass Transfer Processes in Systems Formed by Biofuel Production Components", 2017-2019 (head), No. 21-13-00038 "Critical States in Multicomponent Fluid Systems with Chemical Interaction of Components", 2021-2024 (performer).

Based on the results of the work, **45 articles were published** in international and domestic journals, mainly in the 1st and 2nd quartiles (for the years of their publication).

The work has been validated by presenting its results at the following key conferences: International Conference on Chemical Thermodynamics in Russia – RCCT (2007, 2010, 2011, 2012, 2015, 2019, 2022), International Congress of Chemical and Process Engineering – CHISA (Prague, 2008, 2012, 2016), International Symposium on Solubility Phenomena and Related Equilibrium Processes – ISSP (2008, 2016, 2021, 2022), International Conference on Chemical Thermodynamics – ICCT (2008, 2010), European Symposium on Applied Thermodynamics – ESAT (2008, 2011), International Conference on Solution Chemistry – ICSC (2011, 2013), «Distillation & Absorption» (2006, 2014), World Chemistry Congress (2013), International Scientific Conference of Students, Postgraduates and Young Scientists "Lomonosov" (2019-2022), All-Russian Conference of Young Scientists, Postgraduates and Students with International Participation "Mendeleev" (2012-2014, 2017, 2019), International Conference on Chemistry for Young Scientists “Mendeleev” (2015, 2019, 2021), International Student Conference "Science and Progress (2011-2018, 2020, 2021), Symposium with International Participation "Thermodynamics and Materials Science" (2015, 2018, 2023), All-Russian Conference of Young Chemists (with international participation) in Nizhny Novgorod (2019, 2023).

The thesis consists of an Introduction, a literature review, an experimental section, a discussion of the results, conclusions, acknowledgements, a list of references, is presented on 98 pages, contains 41 figures, 9 tables, the list of references includes 183 sources.

Main scientific results:

- Evaluation of phase behavior features of quaternary systems based on new detailed experimental data on solubility and liquid-liquid equilibrium. Data correlation based on the local composition model (NRTL) equation, using the UNIFAC group model and classical verification methods (Othmer-Tobias, Hand, Marchill, etc.) [60, 92, 62, 61, 57, 41, 76, 86, 50, 91, 29, 40, 51, 67, 20, 110, 39, 87, 85, 58, 45, 33, 34, 107, 11, 42, 109].

- Calculation of thermodynamic and "concentration" constants of chemical equilibrium based on the obtained set of experimental data on chemical equilibrium in systems with reactions of synthesis/hydrolysis of carboxylic acid esters in wide temperature ranges [66, 59, 63, 21, 78, 39, 77, 35, 46, 12, 108, 38, 36, 37, 43, 49].
- A set of experimental results on critical states in multicomponent liquid-phase systems with chemical interaction of the substances that form them [92, 61, 57, 41, 76, 86, 91, 29, 51, 67, 20, 110, 87, 46, 58, 45, 33, 34, 107, 42].
- Polythermal critical surfaces in multicomponent systems with chemical reactions and compositions of chemically equilibrium critical phases [66, 59, 63, 137, 77, 46, 38, 43, 49].
- Derivation of the general equation of the isothermal-isobaric curve of chemical equilibrium. New forms of stability conditions for multicomponent systems with chemical interaction of substances [146, 145, 137].

<u>The main provisions submitted for defense:</u>

- A set of experimental data on phase equilibria in multicomponent liquid-liquid systems (systems of four substances and constituent ternary and binary subsystems) formed by components of mixtures including reagents (reactants) and products of reactions of synthesis and hydrolysis of carboxylic acid esters.
- A set of experimental data on chemical equilibrium in heterogeneous stratifying mixtures of four substances formed by reagents and products of reactions of synthesis and hydrolysis of carboxylic acid esters.
- A set of experimental data on critical states of liquid-liquid equilibrium in systems of four substances with chemical interaction, as well as in the subsystems that form them.
- Results of thermodynamic and topological analysis of the features of multicomponent systems with chemical interaction and critical phases, including the mutual arrangement of critical curves and surfaces, manifolds of phase and chemical equilibrium.
- New forms of thermodynamic conditions of critical state in systems with chemical reactions.

CHAPTER 1. LITERATURE REVIEW: PHASE AND CHEMICAL EQUILIBRIUM, CRITICAL STATES IN MULTICOMPONENT HETEROGENEOUS SYSTEMS WITH CHEMICAL REACTIONS IN LIQUID PHASES

Interest in experimental and theoretical studies of phase equilibria in systems with chemical reactions is due to both the practical significance of reaction-mass-exchange processes for chemical technology and the need to solve fundamental problems of chemical thermodynamics. Combining chemical processes with phase separation allows optimizing the technological process in terms of energy and resource conservation, as well as increasing the environmental friendliness of the technology. Among such practically important processes, one can single out reactive rectification, in which chemical synthesis is accompanied by a vapour-liquid phase transition [1-5], as well as reactive extraction or chemical synthesis in a membrane reactor. A phase transition during a chemical reaction can also play a negative role in technology: it is known that stratification of an initially homogeneous solution during a chemical reaction complicates the control of the synthesis process. At the same time, fundamental studies of combined reaction-mass-exchange processes lead to the establishment of important thermodynamic and kinetic regularities, including those related to the structure of phase diagrams, the mutual arrangement of reaction (stoichiometric) lines, chemical equilibrium manifolds, and isoaffine manifolds [6-8]. Accordingly, the analysis of the structure of phase diagrams of systems with chemical interaction of components requires new theoretical approaches and the formation of a sufficient experimental database.

For the development of fundamental principles of chemical engineering, specific problems of transformation of diagrams of stratified systems with chemical interaction and critical phases (liquid-liquid equilibria) are of interest. Despite the diversity of available data on solubility, liquid-liquid and vapour-liquid equilibria, only a small part of studies relates to the study of reaction systems in a critical state. Most likely, this is due to the dynamic nature of the critical state (nucleation and decomposition), which is significantly complicated in the case of simultaneous chemical processes. At the same time, it is obvious that a set of experimental data on chemical and phase equilibria, critical phases is necessary for the fundamental analysis of the behavior patterns of such complex systems, the establishment of new singularities, as well as for the development of a general theory of critical phenomena in systems with chemical reactions. By the time the research within the framework of this thesis began (2003), detailed and systematic experimental data on critical states in multicomponent systems with chemical interaction were practically absent. Some information was related to studies of liquid-liquid equilibria in systems with chemical reactions, but not specifically to critical states.

Some of the first studies of phase equilibria in systems with chemical reactions were carried out in the 1960s and 1970s at the Department of Solution Theory (Chemical Thermodynamics and Kinetics) of Leningrad University [9, 10] and were, among other things, devoted to the experimental study of vapour-liquid equilibrium in a system with a reaction of ester synthesis [9]. It is these systems (with reactions of synthesis/hydrolysis of carboxylic acid esters) that constitute the absolute majority of the modern experimental database on phase equilibria in reaction mixtures. A detailed analysis is presented in our review articles [11, 12]. Below is a briefer literature review of selected works related to the objects of the thesis. These are, basically, works in which sufficiently complete and suitable material for thermodynamic interpretation was obtained: systems formed by formic, acetic, propionic and oleic acids, methyl, ethyl, propyl, butyl and amyl alcohols, as well as the corresponding ethers and water.

Formic acid - methyl alcohol - methyl formate - water

The system involving methyl formate is one of the first studied systems with the synthesis-hydrolysis reaction of ether, for which studies of simultaneous phase and chemical equilibrium were carried out [9]. Earlier, one of its authors, V. T. Zharov, in his work [10] first proposed transformed concentration variables for representing the thermodynamic properties of systems in a chemical equilibrium state. The derivation of the main relationships was based on the unification of the conditions of chemical and phase equilibrium; thus, the so-called abbreviated fundamental equations were obtained.

Based on the results of our reviews devoted to heterogeneous systems with chemical interaction of components [11, 12], we can note some other works related to the study of this system. In particular, a study of chemical equilibrium was carried out in [13, 14]. In work [15], there are data on vapour-liquid equilibrium. The dependence of temperature and pressure on the composition during the synthesis of methyl formate, i.e. along the reaction (stoichiometric) lines, was studied in [16]. The possibility of stratification during the esterification reaction at 313–333 K was briefly considered there. The article [17] contains the results of calculating chemically equilibrium compositions.

Formic acid - ethyl alcohol - ethyl formate - water

In [18], the kinetics of esterification of formic acid with ethanol was studied in the temperature range of 273.15–309.15 K; the molar ratios of the reactants were varied from 1 to 35; sulfuric acid was used as a catalyst. The experimental values of the reaction rate constant are in good agreement with the calculated results [18]. A method for synthesizing ethyl formate using silica gel as a catalyst with a formic acid to ethyl alcohol ratio of 1:1.48 at a temperature of 341.15–343.15 K was proposed by the authors [19]. Data on phase equilibria in the formic acid–ethanol–ethyl formate–water system are also limited [12]. Liquid–vapor equilibrium in the temperature range of 313–333 K was studied by Tischmeier and Arlt [16]. The changes in temperature, pressure and composition have been determined along some stoichiometric lines, starting from the binary acid-alcohol mixture [16]. As for the studies of solubility and liquid-liquid equilibrium in this quaternary system, detailed experimental data are published in our recent paper [20]; the binodal surfaces in the tetrahedron of compositions at 298.15 K and 308.15 K are also presented there. Some results of the study of chemical equilibrium at 373 K are given in the paper [14]. In our paper [21] a detailed study at 298.15 K is carried out, based on the results of which the location of the chemical equilibrium surface in the concentration tetrahedron is presented. The concentration and thermodynamic constants of chemical equilibrium are determined on the basis of experimental data and the UNIFAC model.

Formic acid – n-propyl alcohol – n-propyl formate – water

The only available data for this reaction system are given in [14]. The work lists 19 chemically equilibrium compositions at 373 K. The effect of changing the amount of water on the concentration constant of equilibrium both in the absence of hydrochloric acid (as a catalyst) and in the presence of very small amounts of it has not been studied in detail. However, it is noted that the concentration constant of equilibrium increases with increasing water concentration. In [14] there are also several references to earlier works. This system is also mentioned in our review [12]. Information on the molar enthalpies of mixing of acid and alcohol is reflected in works [22, 23].

Formic acid – isopropyl alcohol – isopropyl formate – water

There is very limited information in the literature on chemical and phase equilibrium for a system involving isopropyl formate [12]. A study of vapour-liquid equilibrium [16] was conducted at temperatures of 313–353 K. The dependences of temperature, pressure, and composition during a chemical reaction (ether formation) along stoichiometric lines in the concentration space are presented. The data obtained made it possible to illustrate the shift in phase equilibrium when the composition of the binary alcohol-acid mixture changes during the reaction [16]. Some results of the study of chemical equilibrium are presented in [14].

Acetic acid - methyl alcohol - methyl acetate - water

Many works devoted to the study of chemical and phase equilibria in this system are presented in our published reviews [11, 12]. In particular, in [24] data on the vapour-liquid equilibrium for states of chemical equilibrium were published. The authors of [25] determined experimental compositions of the liquid-liquid equilibrium at 293.15, 303, 313 and 323 K at atmospheric pressure. Calculations were performed using the NRTL and UNIQUAC models [25]. Based on the experimental data of [26], the thermodynamic constants of chemical equilibrium in the temperature range of 318.15 – 333.15 K were calculated [26]. Data on the vapour-liquid equilibrium are presented in [27, 28].

Acetic acid – ethyl alcohol – ethyl acetate – water

The acetic acid – ethyl alcohol – ethyl acetate – water system is currently the most studied of the systems in which the esterification-hydrolysis reaction occurs [11, 12]. A review of the works in which the phase equilibrium for this system was studied is presented in our previously published article [29]. An analysis of the literature showed that at present there are many results of studying the solubility in binary and ternary subsystems (from 273.15 K to 363.15 K), but for a quaternary mixture, information on the solubility and liquid-liquid equilibrium is limited compared to the vapour-liquid equilibrium in the case of chemical equilibrium. For example, Bernatova, Aim and Wichterle published data on the vapour-liquid equilibrium for chemically equilibrium states in the acetic acid – ethyl alcohol – ethyl acetate – water system at 348.15 K [30]. Other similar works were carried out by Kang [31] and Kalvar [32] at atmospheric pressure. It should also be noted that the compositions of the critical phases have been determined only in a few papers, in particular, those published by us [29, 33, 34]. Some other references are presented in our review articles [11, 12]. It is necessary to point out our article, in which a study of chemical equilibrium and calculation of the thermodynamic equilibrium constant at 303.15, 313.15 and 323.15 K and atmospheric pressure were carried out [35]. The results [35] were obtained by gas chromatography and nuclear magnetic resonance. The results of a study of chemical equilibrium at 293.15 K are presented in [36-38]. In [37, 38], the features of systems with simultaneous phase and chemical equilibrium are analyzed. Thermodynamic regularities are revealed and the topology of phase diagrams is presented, and thermodynamic conditions for the shift of phase and chemical equilibrium are considered [37, 38]. The values of excess enthalpies for binary mixtures of ethyl alcohol – water and acetic acid – ethyl acetate and for the quaternary system acetic acid – ethyl alcohol – ethyl acetate – water at 313.15 K and atmospheric pressure were obtained in [39]. Similar experiments were carried out for chemically equilibrium mixtures [40] at 313.15 K.

Acetic acid – n-propyl alcohol – n-propyl acetate – water

For the system involving n-propyl acetate, a great deal of detailed experimental data has been obtained, including by the author of the thesis. One of the latest brief reviews of the results of the study of solubility, liquid-liquid equilibrium, and critical phases is given in [41]. We note several works that present data for both binary and ternary subsystems and for the quaternary mixture acetic acid – n-propyl alcohol – n-propyl acetate – water.

Experimental data on solubility at 313.15 K were obtained in [42, 43]. The compositions of the equilibrium liquid-liquid and vapour-liquid phases at the same temperature were determined in [44]. Detailed data on solubility, on the compositions of the coexisting phases, and on the critical states are given in [45] at 293.15 and 303.15 K and atmospheric pressure. A similar study was also carried out at 323.15 and 333.15 K in [41]. The obtained compositions made it possible to present the arrangement of the critical curves formed by the critical points and, consequently, the type of the critical polythermal surface, as well as the binodal surface in the concentration tetrahedron [41]. Of particular interest is the study of chemically equilibrium liquid phases in this system at 293.15 and atmospheric pressure [46]. It is shown that the chemical equilibrium surface belongs to both homogeneous and heterogeneous regions of the compositions under these conditions. In [38], a polythermal critical surface is given containing chemically equilibrium critical points at 293.15, 303.15 and 313.15 K (at the time of publication, in fact, unique data). An experimental study of vapour-liquid equilibrium and chemical equilibrium was carried out in [47]. Phase transitions in the quaternary system are also discussed in [48, 49]. Data on the molar enthalpies of mixing of alcohol and water are reflected in [50].

Acetic acid – n-butyl alcohol – n-butyl acetate – water

A brief review of a number of works devoted to liquid-liquid equilibrium and solubility in the acetic acid – n-butyl alcohol – n-butyl acetate – water system is presented in our article [51]. As a result of this review, inconsistency (inconsistency) of some data in several literature sources was noted. In [51] we also noted articles including studies of chemical equilibrium in this mixture. Despite the importance of these studies for reactive distillation, there are only a few such works in the literature [52-56], not to mention critical phenomena. Work [57] contains information on a comparative analysis of binary subsystems and the results of a comprehensive study of the solubility and compositions of coexisting phases at 328.15 K and atmospheric pressure. The compositions of critical phases have been studied mainly in the works of the author of the thesis and colleagues [51, 56-58]. It is in work [56] that a special chemical equilibrium critical point is discussed, which belongs to the surfaces of chemical and phase equilibrium simultaneously. The results of our studies of chemically equilibrium compositions at 318.15 K and atmospheric pressure are reflected in [59]. The values of excess enthalpies at 313.15 K are given in [60].

Acetic acid – n-amyl alcohol – n-amyl acetate – water

An analysis of the literature data on solubility in the acetic acid – n-amyl alcohol – n-amyl acetate – water system showed that a significant array of experimental compositions has been accumulated over the past eighty years [61]. At the same time, the overwhelming majority of solubility study results relate to binary subsystems. New data on solubility in the temperature range of 273.15 – 453.15 K were published by us in the article [61]. In this work, data are presented on solubility in the quaternary system at 293.15 K, 303.15 K, 313.15 K, 323.15 K and atmospheric pressure. Experiments were conducted under the same conditions to study the equilibrium compositions of coexisting liquid – liquid phases [62].

In general, a significant number of works are devoted to the study of amyl acetate synthesis [63], but only some of them contain data on chemical equilibrium, for example, [12, 64, 65]. The aim of the indicated works is connected with the problems of reactive distillation, therefore the authors determined the simultaneous chemical equilibrium and vapour-liquid equilibrium. The data on the vapour-liquid equilibrium were used to calculate the activity coefficients and the thermodynamic constant of chemical equilibrium [65] at 375.45 – 389.25 K. A number of experimental data on chemically equilibrium compositions at 318.15 K and atmospheric pressure are presented in [63]. It was established that the chemical equilibrium surface corresponds to both homogeneous and heterogeneous regions of compositions. When analyzing the intersection of the chemical equilibrium surface and the critical curve at 318.15 K, the composition of a special critical point belonging to the simultaneous surface of phase and chemical equilibrium was found [63]. An analysis of the type of chemical equilibrium surface for the same system was also carried out in [66], at 323.15 K and atmospheric pressure.

Propionic acid – ethyl alcohol – ethyl propionate – water

A very limited number of studies have been devoted to the study of solubility, liquid–liquid equilibrium, and chemical equilibrium in this system [67]. The first data on the solubility and critical point in the ternary system ethyl alcohol – ethyl propionate – water were obtained in 1910 by Bonner [68] at 273.15 K and atmospheric pressure using the pycnometric method. Mutual solubility in the binary system ethyl propionate – water was determined at 298 K in [69], including calorimetry and differential refractometry methods. Some data on solubility in the same system were presented by Venkataran, Rao, and others [70–72] at 302.15 – 303.15 K. Data on the liquid–liquid equilibrium over a wide temperature range, 273 – 353 K, are presented in [73]; in the article [74] – for temperatures of 293.15 – 353.15 K. Recommended values of data on mutual solubility in the ethyl propionate – water system are collected in [75]. The compositions of coexisting phases for binary and ternary subsystems are given in [76] at 293.15 K and 303.15 K.

In the work published by us earlier [77], data on chemical equilibrium were obtained at 303.15 and 313.5 K and atmospheric pressure. It was shown that chemical equilibrium is achieved both in the homogeneous and heterogeneous regions of the reaction mixture composition. The study was also conducted at 293.15 K (data published in the article [78]). Apart from the above results (works [77] and [78]), the only experimental data on the properties of the propionic acid – ethyl alcohol – ethyl propionate – water system were presented in 1982 by Macedo and Rasmussen [79]. The liquid – vapor equilibrium was determined for a mixture of ethyl propionate and propionic acid at 358 and 368 K and a pressure of 134.28 – 573.05 mm Hg for 20 binary mixture compositions. The data were compared with the compositions calculated using the UNIFAC model.

Propionic acid – n-propyl alcohol – n-propyl propionate – water

The first results of the study of the solubility of n-propyl propionate in water were presented by Hemptinn in 1894 [80], at 298 K, and in the thesis of Reimann in 1906 [81], at 273.15 – 303.15 K and 101.325 kPa. The compositions of the coexisting phases in this binary system were determined in [82] in the temperature range of 273 – 363 K and atmospheric pressure. Using the isothermal (at 293 K) titration method, data on the mutual solubility in the n-propyl propionate – water binary system were obtained by Mozzhukhin et al. in [83]. The same method was used to determine the solubility at 293.15 – 353.15 K and 101.325 kPa in [74]. The solubility data recommended by Getzen, Hefter and Machinski for the same two-component system are collected in [75]. The number of works devoted to the study of liquid-liquid equilibria in the ternary subsystems n-propyl alcohol-n-propyl propionate-water and propionic acid-n-propyl propionate-water is also limited. There are solubility data obtained by titration for the ternary system with alcohol at 293 K [83] and at 288.15 K [84]. As for the quaternary system propionic acid – n-propyl alcohol – n-propyl propionate – water, the data for it are published only in our articles [85, 86], at several temperatures, 293.15, 303.15, 313.15 and 333.15 K, including detailed information on the compositions of the liquid – liquid equilibrium phases for binary and ternary subsystems. In addition, the article [86] presents the results of a detailed study of the critical phases at 303.15 K.

Propionic acid – n-butyl alcohol – n-butyl propionate – water

Compared with liquid–vapor equilibrium and kinetic studies, liquid–liquid equilibrium data for the n-butyl propionate synthesis reaction are more limited [87]. The coexisting phase compositions for two binary systems, n-butanol–water and n-butyl propionate–water, are given in [88]. The NRTL model was used to compare mutual solubility data for the binary subsystems in the work of Lee et al. [89]. The results of liquid–liquid phase equilibrium calculations for the ternary system n-butanol–n-butyl propionate–water using the NRTL model are also presented in [90]. The most complete and detailed information on the phase behavior of the quaternary system propionic acid – n-butyl alcohol – n-butyl propionate – water and on the critical compositions is given in our works: at 293.15 K [91] and at 303.15 K [87].

Oleic acid – methyl alcohol – methyl oleate – water

An analysis of the literature [92] shows that data on the liquid-liquid equilibrium for the oleic acid-methanol-methyl oleate-water system are extremely scarce. Chen et al. [93] experimentally studied the phase equilibrium for the oleic acid-methanol-methyl oleate-water system at 346.15 K during a chemical reaction and the establishment of chemical equilibrium. The oleic acid content in the test samples was determined by titration with potassium hydroxide, and the methanol and methyl oleate content was determined by gas chromatography. It is indicated that adding excess alcohol to the reaction mixture during the esterification of fatty acids with methanol can lead to the formation of a two-phase liquid system. The authors studied the possibility of using this phenomenon to remove water formed as a result of esterification without the use of dehydrating agents, and thus increasing the yield of methyl oleate. An algorithm for calculating the compositions of the coexisting phases of the reacting mixture is proposed. The UNIQUAC model was used for the calculations. The paper [94] presents the results of a study of the liquid-liquid equilibrium in the ternary system methanol-methyl oleate-water at 298.2 K, 308.2 K and 318.2 K and atmospheric pressure. The equilibrium compositions of the coexisting liquid phases were determined by gas chromatography. In the region of critical compositions, the solubility limit was studied by turbidity titration. The corresponding phase diagrams are presented. The experimental data were compared with calculations using the UNIFAC, UNIQUAC and NRTL models. The UNIQUAC method yielded the best results (discussed in detail for 298.2 K). The mutual solubility of water and oleic acid at temperatures from 522.3 K to 589.9 K and pressures from 4.51 MPa to 11.49 MPa was studied in [95]. The composition of the phase rich in oleic acid was determined by titration using the Fischer method. The composition of the water-enriched phases was analyzed by gas chromatography. It was found that the system has an upper critical point, its composition, critical temperature and pressure were determined. The critical point was recorded by observing the critical opalescence both with a slow increase in temperature in the heterogeneous region and with a decrease in temperature (in the homogeneous region). Experimental data on the binodal and the critical point are presented in the phase diagram. The study of solubility, critical states and liquid-liquid equilibrium in the oleic acid – methanol – methyl oleate – water system, its ternary and binary subsystems at 303.15 K and atmospheric pressure was carried out in [92]. The compositions for the binodal curves and the solubility surface were determined by the cloud point method. The compositions of the equilibrium liquid-liquid phases were determined using NMR spectroscopy. The experimental results are presented graphically on phase diagrams in concentration simplices, including a three-dimensional phase diagram in a composition tetrahedron. A comparative analysis of the available literature data was performed. The correlation and prediction of the experimental data on liquid-liquid equilibrium were performed using the NRTL and UNIFAC models, respectively. It was noted that the modeling results are in satisfactory agreement with the experimental data.

CHAPTER 2. EXPERIMENTAL PART

2.1. Selection of objects of experimental research

As already noted, the interest in the study of combined reaction-mass transfer processes is due to both their practical significance for chemical technology and the need to solve new fundamental problems of chemical thermodynamics. These works are of particular importance for the development of fundamental and applied aspects of the theory of reaction-mass transfer processes [96, 97]. Despite the well-known interest in such studies, the volume of experimental material accumulated over the past decades is relatively small in comparison with data on equilibria in systems without chemical interaction of components. First of all, this is due to the limited possibility of choosing experimental objects convenient for subsequent theoretical interpretation of the obtained data, as well as to additional technical difficulties that arise when studying reaction systems. Thus, a shift in the composition of the mixture as a result of a chemical reaction when determining the parameters of phase equilibrium can lead to significant experimental errors. Obviously, the specificity of the reaction system determines some of its additional features, reflected, in particular, in the structure of the state diagrams. The diagram of a multicomponent reaction system, in comparison with systems without reactions, includes such varieties as reaction (stoichiometric) lines and isoaffin surfaces and hypersurfaces. These features, in particular, are important for the organization of such technologically important combined processes as reactive rectification and reactive extraction. Most of the works in the field of phase equilibria in systems with chemical interaction of components were carried out for homogeneous systems, while, as indicated in the Introduction, the vapour-liquid equilibrium was investigated. Accordingly, the choice of objects of the thesis was aimed at new problems, systems with solution stratification and chemical reactions. It should be noted that the thermodynamic laws for both types of systems are largely the same, which makes it possible to directly apply a number of results obtained for vapour-liquid reaction systems to liquid-liquid systems with chemical interaction. The choice of objects of study was also associated with theoretical problems, the development of approaches based on the results obtained about forty to fifty years ago and in subsequent years mainly by domestic scientists - L. A. Serafimov, V. T. Zharov and co-workers [96, 98-101]. Among similar works, one can also note the articles of Docherty and co-workers [102, 103] and a number of other studies [104, 105].

Thus, the object of the thesis research is reactionary multicomponent mixtures with limited solubility of components. In the studied systems of four substances, chemical reactions of esterification-hydrolysis occur. The thesis also sets the tasks of experimental study of solubility, phase equilibrium and critical states in the absence of chemical interaction of components, as well as chemical equilibrium. Since experimental data on critical phenomena in chemically reacting environments are currently few, new experimental results are also necessary for the development of approaches to thermodynamic analysis of the features of the critical state in chemically reacting environments. The last sections of the thesis are devoted directly to theoretical thermodynamic analysis. Accordingly, the choice of objects of the thesis research should allow to expand the methods of phenomenological thermodynamics of the critical state, as well as to replenish the fundamental base of experimental data on phase and chemical transformations in reactive stratifying systems. The specific objects of the study are mixtures containing an acid, an alcohol, the corresponding ether, and water, namely: acetic acid – n-propyl alcohol/n-butyl alcohol/n-amyl alcohol – n-propyl acetate/n-butyl acetate/n-amyl acetate – water, propionic acid – ethyl alcohol/n-propyl alcohol/n-butyl alcohol – ethyl propionate/n-propyl propionate/n-butyl propionate – water, and oleic acid – methyl alcohol – methyl oleate – water. All experiments were carried out under isothermal conditions and atmospheric pressure. The possibility of neglecting the effect of pressure is associated with known regularities: small changes in pressure have virtually no effect on the values of the chemical potentials of substances in condensed phases. Specific systems and data on them, in addition to their fundamental significance, are of interest, in particular, for the design of various chemical-technological processes in the synthesis and purification of industrially significant esters (n-propyl acetate, n-butyl acetate, n-amyl acetate, ethyl propionate, n-propyl propionate, n-butyl propionate and methyl oleate).

2.2 Preparation and purification of reagents

The reagents – components of the studied systems – in accordance with the manufacturers' instructions, had a sufficiently high degree of purity: n-propyl acetate (> 0.99 mol. dol., Sigma-Aldrich and > 0.98 mol. dol., Vecton), propionic acid (> 0.98 mol. dol., Vecton and > 0.99 mol. dol., BASF), n-butyl acetate, n-amyl acetate, acetic acid, ethyl propionate, n-propyl alcohol, n-butyl alcohol, n-amyl alcohol (> 0.98 mol. dol., Vecton), n-propyl propionate and n-butyl propionate (> 0.99 mol. dol., Sigma-Aldrich), ethyl alcohol (> 0.96 mol. dol., Vecton), oleic acid (> 0.94 mol. dol., Saveo), methyl alcohol (> 0.99 mol. dol., Vecton), methyl oleate (> 0.97 mol. dol., Thermo Scientific). However, all substances were rechecked for purity, and additional purification was carried out for most of them. The main method was distillation on rectification columns with an efficiency of 25-30 theoretical plates. Ethyl alcohol was dried using molecular sieves. In the case of oleic acid, vacuum distillation was used. Water was distilled twice. Purity control after purification was carried out by gas chromatography and refractometry (IRF454B2M refractometer, the indicators were compared with NIST data [106]). According to the results of gas chromatographic analysis (Crystal 5000.2M and Shimadzu GC-2010 Plus), as well as chromatograph mass spectrometry (for oleic acid and methyl oleate) (Shimadzu GCMS-QP 2010 Plus), the purity of all substances was sufficient for conducting phase equilibria experiments (Table 1). The main impurity in the indicated reagents was water, a component of all studied systems, and its content (<0.01 mol. fraction) was taken into account when preparing the initial solutions. A more detailed description of the preparation and purification of reagents, purity control for each of the systems is presented in the corresponding publications (references are given in the subsections, when characterizing the results and data for the indicated systems).

Table 1. Purity of reagents

Substance	Supplier	Initial purity value[a]	Purification Method	The final value of purity[a]	Method of analysis
acetic acid	Vecton	0.980	rectification	0.995	gas chromatography
propionic acid	Vecton BASF	0.980 0.990	rectification -	0.990 0.990	gas chromatography
oleic acid	Saveo	0.940	fractional distillation	0.990	chromatography-mass spectrometry
methyl alcohol	Vecton	0.995	-	0.995	gas chromatography
ethanol	Vecton	0.960	molecular sieves	0.990	gas chromatography
n-propyl alcohol	Vecton	0.990	rectification	0.995	gas chromatography
n-butyl alcohol	Vecton	0.980	rectification	0.995	gas chromatography
methyl oleate	Thermo Scientific	0.970	-	0.970	chromatography-mass spectrometry
n-propyl acetate	Sigma-Aldrich Vecton	0.990 0.980	- rectification	0.990 0.995	gas chromatography
n-butyl acetate	Vecton	0.980	rectification	0.995	gas chromatography
n-amyl acetate	Vecton	0.990	rectification	0.995	gas chromatography
ethyl propionate	Vecton	0.980	rectification	0.995	gas chromatography
n-propylpropionate	Sigma-Aldrich	0.990	-	0.990	gas chromatography
n-butyl propionate	Sigma-Aldrich	0.990	-	0.990	gas chromatography
water	-	0.999	bidistillation	0.999	gas chromatography

[a] The standard deviation was 0.005 mole fractions

2.3. Methods of quantitative analysis of phase compositions and chemical equilibrium compositions

2.3.1. Gas chromatographic analysis

To analyze the phase compositions and chemically equilibrium mixtures, an individual gas chromatographic mode was selected (Table 2), ensuring optimal separation of chromatographic peaks and their quantitative interpretation (by internal normalization or internal standard methods). Two chromatographs with thermal conductivity detectors (katharometers) were used in the work: Crystal 5000.2M and Shimadzu GC-2010 Plus. Helium grade "A" was used as a carrier gas. Gas chromatographic columns: Porapak R, Porapak QS, HP-FFAP, Restek Rt-Q-Bond. The error of gas chromatographic analysis on average did not exceed 0.005 mole fractions.

Table 2. Gas chromatographic modes for the studied systems

Chromatograph	Column and column temperature	Evaporator/ thermal conductivity detector temperature	Carrier gas flow rate, ml/min	Equilibrium type, temperature	Reference
acetic acid – n-propyl alcohol – n-propyl acetate – water					
Crystal 5000.2M	Porapak R 473.15 K	503.15/493.15 K	60	Liquid-liquid equilibrium, 323.15 K and 333.15 K	[41]
Crystal 5000.2M	Porapak R 468 K	503/513 K	60	Liquid-liquid equilibrium, 293.15 K and 303.15 K	[45]
Crystal 5000.2M	Porapak R 453.15 K	503/513 K	30	Liquid-liquid equilibrium, 293.15 K, 303.15 K and 313.15 K	[107] (n-propyl alcohol – n-propyl acetate – water)
Crystal 5000.2M	Porapak R 453.15	503/513 K	30	Chemical equilibrium and simultaneous chemical and phase equilibrium, 303.15 K	[108]
Crystal 5000.2M	Porapak R 200°C	230/220°C	60	Chemical equilibrium and simultaneous phase and chemical equilibrium, 293.15 K. Chemical equilibrium, 353.15 K. Liquid-liquid equilibrium, 353.15 K	[46]

Crystal 5000.2M	Porapak R 180°C	230/240°C	30	Liquid-liquid equilibrium, 293.15 K, 303.15 K and 313.15 K	[109] (acetic acid – n-propyl acetate – water)
acetic acid – n-butyl alcohol – n-butyl acetate – water					
Crystal 5000.2M	Porapak R 483 K	503/513 K	60	Liquid-liquid equilibrium, 308.15 K	[58]
Shimadzu GC-2010 Plus	HP-FFAP from 373.15 K to 473.15 K (10 K in 1 min)	523.15/523.15 K	2	Liquid-liquid equilibrium, 328.15 K	[57]
Crystal 5000.2M	Porapak R 483.15 K	503.15/513.15 K	30	Liquid-liquid equilibrium, 318.15 K	[51]
Shimadzu GC-2010 Plus	HP-FFAP from 373.15 K to 473.15 K (10 K in 1 min)	523.15/523.15 K	2	Chemical equilibrium and simultaneous chemical and phase equilibrium, 328.15 K	[59]
acetic acid – n-amyl alcohol – n-amyl acetate – water					
Shimadzu GC-2010 Plus	HP-FFAP 373.15 K	523.15/523.15 K	2	Chemical equilibrium and simultaneous chemical and phase equilibrium, 318.15 K	[63]
Shimadzu GC-2010 Plus	Restek Rt-Q-Bond from 200°C to 250°C (10°C in 1 min)	250/250°C	20.8	Chemical equilibrium and simultaneous chemical and phase equilibrium, 323.15 K	[66]
Shimadzu GC-2010 Plus	HP-FFAP from 373.15 K to 473.15 K (10 K in 1 min)	523.15/523.15 K	37.7	Liquid-liquid equilibrium, 293.15 K, 303.15 K, 313.15 K and 323.15 K	[62]
Crystal 5000.2M	Porapak R 503.15 K	503.15/513.15 K	60	Liquid-liquid equilibrium, 303.15 K	[110]
Crystal 5000.2M	Porapak R from 373.15 K to 473.15 K (10 K in 1 min)	503.15/513.15 K	60	Liquid-liquid equilibrium, 293.15 K, 303.15 K, 313.15 K and 323.15 K	[61] (n-amyl alcohol – water and n-amyl acetate – water)

propionic acid – ethyl alcohol – ethyl propionate – water					
Crystal 5000.2M	Porapak R 483.15 К	503.15/513.15 К	60	Simultaneous chemical and phase equilibrium, 303.15 K and 313.15 K	[77]
Crystal 5000.2M	Porapak R 473.15 К	503.15/513.15 К	30	Liquid-liquid equilibrium, 293.15 K and 303.15 K	[76] (propionic acid – ethyl propionate – water and ethyl alcohol – ethyl propionate – water)
Crystal 5000.2M	Porapak R 483.15 К	503.15/513.15 К	60	Simultaneous chemical and phase equilibrium, 293.15 K	[78]
propionic acid – n-propyl alcohol – n-propyl propionate – water					
Crystal 5000.2M	Porapak R 483.15 К	503.15/513.15 К	60	Liquid-liquid equilibrium, 293.15 K, 313.15 K and 333.15 K	[85]
Crystal 5000.2M	Porapak QS 483.15 К	503.15/503.15 К	60	Liquid-liquid equilibrium, 303.15 K	[86]
propionic acid – n-butyl alcohol – n-butyl propionate – water					
Crystal 5000.2M	Porapak R 463.15 К	503.15/513.15 К	60	Liquid-liquid equilibrium, 303.15 K	[87]
Crystal 5000.2M	Porapak R from 468.15 К to 483.15 К (2 К in 1 min)	503.15/513.15 К	30	Liquid-liquid equilibrium, 293.15 K	[91]

In studying the liquid-liquid phase equilibrium in quaternary systems and constituent ternary and binary subsystems, we mainly used the traditional method. Heterogeneous (stratifying) mixtures of a given gross composition were prepared in glass vials (volume 5-10 ml) on Pioneer OHAUS PA214 (0.0001 g) and Shinko VIBRA HT-120CE (0.001 g) analytical balances. The compositions of the mixtures were selected taking into account the most complete representation of the phase equilibrium in the concentration simplex. In particular, the gross compositions of the quaternary mixtures belonged to the cutting planes uniformly located in the concentration tetrahedron. Then the solutions, in already closed vials (with a special stopper, providing the possibility of sampling in the future), were brought to a given temperature (LOIP LT-105 thermostat, ± 0.05 K). After mixing (with a magnetic stirrer) and subsequent stratification, samples of each phase were collected directly with a chromatographic syringe (Hamilton, 1 μl and 10 μl), preheated to a higher temperature (to avoid sample stratification in the syringe). Samples were collected after complete phase separation: the criterion was the transparency of the layers of the heterogeneous mixture. Then the sample was introduced into the chromatograph, also under temperature conditions that excluded sample stratification. Sufficient volumes of vials and initial solutions made it possible to repeat (three times or more) sample collections for additional control of the determined phase compositions.

A more detailed presentation of the features of determining phase equilibrium in specific systems is presented in the relevant publications (references are given in subsections, when characterizing the data for each system). When studying chemical equilibrium in a homogeneous and heterogeneous region, the studies were carried out in a similar way: in thermostatted vials tightly closed with a special lid with the possibility of sampling. To accelerate the esterification reaction, if necessary, a catalyst was added (1-2 drops of 36.5% hydrochloric acid). The time to achieve chemical equilibrium depended on the substances of the system, composition and temperature, and averaged from 4 to 30 days. To monitor the progress (completion) of the chemical reaction, samples were periodically taken for their gas chromatographic analysis. The constancy of the system composition was a criterion for the completion of the reaction, the establishment of chemical equilibrium.

Some features are related to chemical equilibrium in a heterogeneous region. For example, if during (as a result of) a chemical reaction the initial homogeneous mixture of reactants was stratified, then, as in the case of phase equilibrium studies, it was stirred for 4–30 days (depending on the composition and temperature). Stirring was stopped periodically, phase equilibrium was established (transparency of the phases), and samples of the phases were taken for chromatographic analysis. The criterion for the onset of chemical equilibrium was also the constancy of the composition.

The specifics of determining chemical equilibrium in specific systems are presented in the relevant publications (references are also given in the subsections, when characterizing the data for each system).

2.3.2. NMR analysis

In addition to the traditional gas chromatographic method, the thesis alternatively used the nuclear magnetic resonance method. The systems for which we used the NMR analysis method were propionic acid – ethyl alcohol – ethyl propionate – water (chemical equilibrium, homogeneous compositions) [77, 78] and oleic acid – methyl alcohol – methyl oleate – water (phase equilibrium) [92].

The method of studying chemically equilibrium homogeneous mixtures, their analysis by the 1H NMR method for the propionic acid – ethyl alcohol – ethyl propionate – water system is as follows: the initial solutions of known composition were prepared gravimetrically in glass vials (5 ml) on a Shinko VIBRA HT-120CE analytical balance with an accuracy of 0.001 g. 36.5% hydrochloric acid in an amount of 0.003 mol. dol. The vials were tightly sealed with a stopper and placed in a LOIP LT-105 liquid thermostat (± 0.05 K) at a constant temperature. Chemical equilibrium was considered to be achieved (on average 4 days depending on the thermostatting temperature) if the composition of the analyzed mixture did not change. Then, samples were taken from the vials, placed in ampoules for NMR analysis and analyzed on a Bruker AVANCE III NMR spectrometer with a frequency of 500 MHz. The baseline correction was performed automatically. Well-separated peaks of CH2- and CH3-groups of each compound in solution were used for integration (quantitative interpretation of NMR spectra). The standard uncertainty of 1H NMR analysis was 0.005 mol. dol. The author expresses gratitude to the staff of the Resource Center of St. Petersburg

State University "Magnetic Resonance Research Methods" for their assistance in conducting these studies and interpreting the NMR spectra.

The same method of analysis was used to study the liquid-liquid equilibrium of binary (oleic acid – water and methyl oleate – water) and ternary subsystems oleic acid – methanol – water, methanol – methyl oleate – water and oleic acid – methyl oleate – water. The initial heterogeneous mixtures were prepared gravimetrically in glass vials (3 ml) on a Pioneer OHAUS PA214 analytical balance (0.0001 g). Then these mixtures in tightly closed vials were stirred for 30 min and kept in a liquid thermostat until complete distribution of the phases and their transparency were achieved, which was an additional criterion of equilibrium. The time to establish phase equilibrium was on average 6 hours. Next, a sample was taken from each phase using a heated (slightly above the experimental temperature) 0.5 ml dispenser and placed in NMR ampoules containing 2 ml of acetone (to maintain homogeneity of the phase samples in case of their possible stratification as a result of a decrease in temperature). The analysis of the samples, as in the case of the chemical equilibrium study, was carried out on a Bruker AVANCE III NMR spectrometer. The error in determining the composition was on average 0.005 mole fractions.

2.4. Methodology for studying solubility

The solubility study for all quaternary systems, ternary and binary subsystems was carried out by titration for "turbidity/clarification" ("cloud-point technic", isothermal titration). A special setup for these purposes consisted of a thermostat, a thermostatted glass cell with a titrated mixture, a magnetic stirrer for stirring, a microburette or a syringe for titration. The initial homogeneous or heterogeneous mixtures of known composition were prepared gravimetrically on Pioneer OHAUS PA214 (0.0001 g) and Shinko VIBRA HT-120CE (0.001 g) analytical balances. The mixtures were titrated at a constant temperature maintained by a LOIP LT-105 liquid thermostat (± 0.05 K) until the second phase was formed ("turbidity" titration) or until the titrated solution was completely homogenized ("clarification" titration). The point corresponding to solubility, i.e. the point on the binodal, was thus fixed. Then the composition was calculated based on the amount and composition of the initial solution and the amount of titrant spent. The estimated titration error averaged 0.005 mole fractions.

In most cases, titration with water and ethers was carried out in "turbidity" experiments, and with acids and alcohols in "clarification" experiments. The initial compositions were selected to provide the most complete picture of solubility in the system. In particular, in the case of quaternary systems, as in the study of phase compositions, the initial compositions belonged to the ordered intersecting planes of the concentration tetrahedron.

Note that phase equilibrium data, as is known, also include solubility data. At the same time, the procedure for applying the cloud-point technic, the process of isothermal titration, provides more accurate data, especially near the near-critical region, compared to gas chromatographic analysis. On the other hand, such a determination of solubility does not allow one to determine the compositions of **coexisting** phases. Thus, a combination of both, virtually independent, methods provides higher quantitative accuracy of the data.

The specifics of determining solubility in specific systems are presented in the relevant publications (references are given in the subsections, when characterizing the data for each system).

2.5. Determination of the compositions of critical phases

In accordance with the main topic of the thesis, the experimental study of critical states was given central attention. A certain complexity was introduced by the features of multicomponent systems, since the critical phases formed in them are no longer "critical points" but critical manifolds, i.e. curves and surfaces. In the case of simultaneous chemical and phase equilibrium, critical manifolds on the surface of chemical equilibrium should be considered. These features increase the labor intensity, or rather, the volume of experiments (data), but, nevertheless, allow the use of known traditional approaches. Thus, in the study of critical states, a set of methods was used that combine direct definition and calculation, and also take into account the features of these states.

- The appearance of opalescence, usually blue and of varying intensity, was taken into account.
- The composition of the critical phase (phases) was determined as a result of a series of solubility experiments. In this case, in the near-critical region, the transparent solution acquires a white "color", and in the critical state, blue critical opalescence is observed.
- The composition of the critical phase (phases) was additionally determined from the data on the liquid-liquid phase equilibrium by extrapolating the data (the College graphical method to the "zero length" tie-line (critical point).
- The composition of the chemically equilibrium critical phase (phases) was determined by extrapolating the data on the "chemically equilibrium liquid-liquid tie-lines" to the zero length tie-line (chemically equilibrium critical point). In quaternary systems, these tie-lines form a ruled surface on the chemical equilibrium surface as a whole, i.e. including a homogeneous and heterogeneous region.

The study of solubility in determining the compositions of critical phases was carried out using the same "cloud-point technique" (isothermal titration) method, on the setup and equipment described above (section 2.4). The composition of the initial solutions was selected in accordance with the approximate composition of the critical phase, according to the liquid-liquid equilibrium data. The titration procedure for determining the critical phase in ternary systems did not present any particular difficulties. In the case of quaternary systems, it was necessary to conduct a large series of experiments in "search" for the critical state: the isothermal critical curve. For this, just as in the experiments described above (liquid-liquid, solubility), certain sections of the concentration tetrahedron were selected, where presumably, in particular, according to the liquid-liquid equilibrium data, the critical state can be realized. The remaining elements of the method corresponded to those described above (for determining solubility and liquid-liquid equilibrium): solutions were prepared on Pioneer OHAUS PA214 (0.0001 g) and Shinko VIBRA HT-120CE (0.001 g) analytical balances, the temperature regime was maintained with a LOIP LT-105 liquid thermostat (± 0.05 K). The error in determining critical compositions is estimated at an average of ± 0.005 mole fractions. The features of determining the compositions of critical phases and chemically equilibrium critical states in specific systems are presented in the relevant publications and in the cited articles on the thesis material (references are given in the subsections, when characterizing the data for each system).

2.6. Experimental results

2.6.1. The system acetic acid – n-propyl alcohol – n-propyl acetate – water

The results of the study of chemical equilibrium (synthesis/hydrolysis reactions of n-propyl acetate) at several temperatures in the homogeneous (293.15 K and 303.15 K) and heterogeneous (293.15 K and 303.15 K) composition ranges are published in [46, 108]. The chemical equilibrium surface in the composition tetrahedron, in accordance with the reaction equation, is located inside the concentration simplex and “rests” on the edges of the tetrahedron, corresponding to four binary subsystems without chemical interaction: water – alcohol, water – acid, ether – alcohol, ether – acid. The remaining binary subsystems (water – ether and alcohol – acid), like all ternary subsystems, are chemically nonequilibrium and cannot belong to the chemical equilibrium surface. The illustration is shown in Fig. 2.6.1.1.

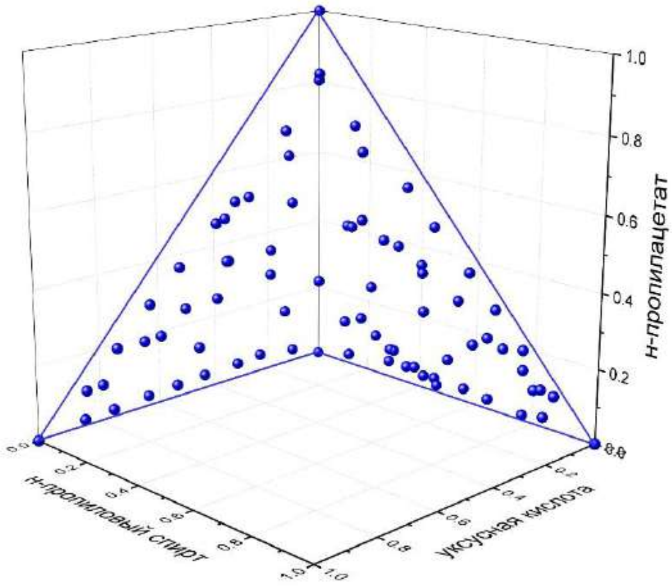

Fig. 2.6.1.1. Surface of chemical equilibrium for the system acetic acid – n-propyl alcohol – n-propyl acetate – water (● - homogeneous compositions) at 303.15 K and atmospheric pressure [108] (mole fractions).

The phase structure of the equilibrium diagrams is determined by the separation in the binary system water – ether. Accordingly, the separation regions in two ternary subsystems including water and ether (acetic acid – n-propyl acetate – water and n-propyl alcohol – n-propyl acetate – water) and the binodal curves are closed on the sides of the triangles of compositions corresponding to the binary system water – ether. In the quaternary system, the separation region is a part of the volume of the tetrahedron of compositions limited by the binodals in the indicated ternary subsystems. Inside the tetrahedron, this region is limited by the binodal surface on which the critical curve is located. The illustration is shown in Fig. 2.6.1.2.

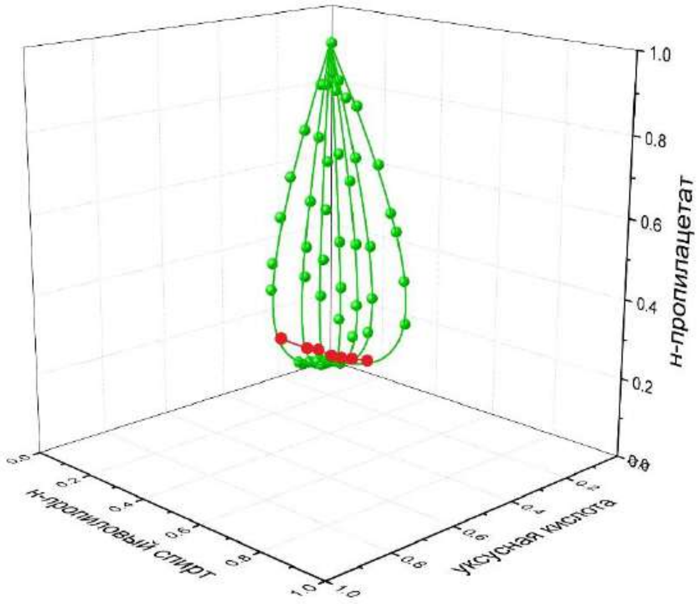

Fig. 2.6.1.2. Binodal surface (● – compositions belonging to the phase equilibrium surface [45, 108]) and the critical curve formed by the critical points (●) [45], or the system acetic acid – n-propyl alcohol – n-propyl acetate – water at 303.15 K and atmospheric pressure (mole fractions).

The characteristics and scope of the studies conducted are presented in Table 3. Specific data and results with reference to our published works:

- Results of solubility studies at different temperatures (293.15 K, 303.15 K, 313.15 K, 323.15 K and 333.15 K) [41, 42, 45, 107, 109].
- Results of liquid-liquid equilibrium studies (compositions of coexisting phases) at different temperatures (293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K and 353.15 K) [41, 45, 46, 107, 109]. - Results of the study of critical phases, critical compositions in chemically equilibrium (313.15 K) [42] and nonequilibrium (293.15 K, 303.15 K, 313.15 K, 323.15 K and 333.15 K) [41, 42, 45, 107, 109] states.
- Chemically equilibrium compositions for homogeneous and heterogeneous mixtures (293.15 K, 303.15 K and 313.15 K) [42, 46, 108].

Table 3. Information on the studies of the system acetic acid – n-propyl alcohol – n-propyl acetate – water in the thesis

Type of research	**Temperature, K, 1 атм**	**Published**
The system acetic acid – n-propyl alcohol – n-propyl acetate – water		
Liquid-liquid equilibrium	293.15, 303.15	[45]
Liquid-liquid equilibrium and compositions of chemically equilibrium phases	293.15	[46]
Liquid-liquid equilibrium and compositions of chemically equilibrium phases	303.15	[108]
Liquid-liquid equilibrium	323.15, 333.15	[41]
Liquid-liquid equilibrium	353.15	[46]
Solubility	293.15, 303.15	[45]
Solubility	313.15	[42]

Solubility	323.15, 333.15	[41]
Critical states	293.15, 303.15	[45]
Critical states and chemically equilibrium critical phases	313.15	[42]
Critical states	323.15, 333.15	[41]
Chemical equilibrium	303.15, 313.15	[42, 46, 108]
Ternary subsystem acetic acid – n-propyl acetate – water		
Liquid-liquid equilibrium	293.15, 303.15	[45, 109]
Liquid-liquid equilibrium	313.15	[109]
Liquid-liquid equilibrium	323.15, 333.15	[41]
Solubility	293.15, 303.15	[45, 109]
Solubility	323.15, 333.15	[41]
Critical states	293.15, 303.15	[45, 109]
Critical states	313.15	[42]
Critical states	323.15, 333.15	[41]
Ternary subsystem n-propyl alcohol – n-propyl acetate – water		
Liquid-liquid equilibrium	293.15, 303.15	[45, 107]
Liquid-liquid equilibrium	313.15	[107]
Liquid-liquid equilibrium	323.15, 333.15	[41]
Liquid-liquid equilibrium	353.15	[46]
Solubility	293.15, 303.15	[107]
Solubility	313.15	[42]
Solubility	323.15, 333.15	[41]
Critical states	293.15, 303.15, 313.15	[45, 107]
Critical states	323.15, 333.15	[41]
Binary subsystem n-propyl acetate – water		
Liquid-liquid equilibrium	293.15, 303.15, 313.15	[107, 109]
Liquid-liquid equilibrium	323.15, 333.15	[41]
Liquid-liquid equilibrium	353.15, 333.15	[46]
Solubility	293.15, 303.15	[45, 107, 109]
Solubility	313.15 K	[107, 42]

2.6.2. The system acetic acid – n-butyl alcohol – n-butyl acetate – water

Unlike the previous system, the phase structure of the equilibrium diagrams is determined by the separation in two binary systems, n-butyl alcohol – water and n-butyl acetate – water. Accordingly, the separation regions already include three ternary subsystems: acetic acid – n-butyl acetate – water, n-butyl alcohol – n-butyl acetate – water, acetic acid – n-butyl alcohol – water. In the ternary system acetic acid – n-butyl alcohol – n-butyl acetate there is no separation. In the system n-butyl alcohol – n-butyl acetate – water two binary systems separate and the immiscibility region has the form of a strip. In the other systems, acetic acid – n-butyl acetate – water and acetic acid – n-butyl alcohol – water, the separation regions are limited by the ether – water system, the binodal is closed on this side of the composition triangle. In the quaternary system, the stratification region is a segment of an ellipsoidal toroid. Inside the tetrahedron, this region is bounded by a binodal surface that rests on two edges of the concentration tetrahedron, corresponding to binary subsystems with limited solubility: n-butyl acetate – water and n-butyl alcohol – water. The illustration presented in Fig. 2.6.2.1 contains the results of a study of the compositions of coexisting phases for binary mixtures, solubility data for the entire system over the entire concentration range, and information on the critical phases at 318.15 K [51].

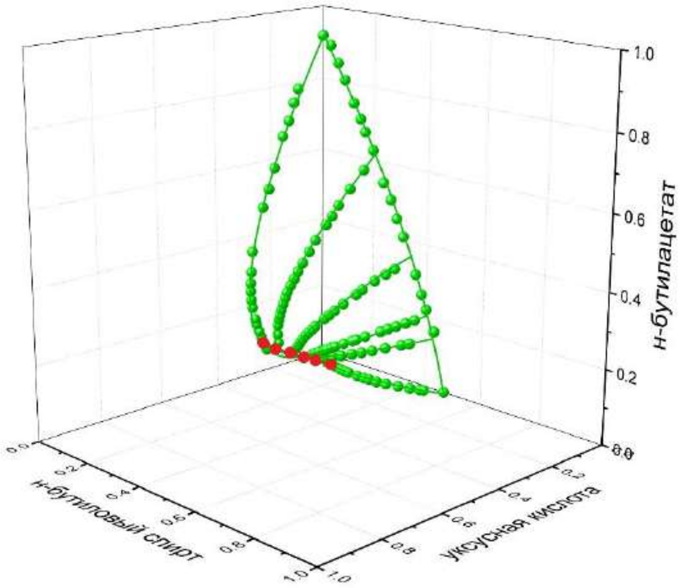

Fig. 2.6.2.1. Binodal surface (● – compositions belonging to the phase equilibrium surface [51]) and the critical curve formed by the critical points (●) [51], or the system acetic acid – n-butyl alcohol – n-butyl acetate – water at 318.15 K and atmospheric pressure (mole fractions).

Chemical equilibrium in this system for both homogeneous and heterogeneous compositions was studied at 318.15 K [59]. Previously, the department conducted studies of chemically equilibrium compositions at 308.15 K [56].

The characteristics and scope of the studies are given in Table 4. Specific data and results with reference to our published works:

- Results of studying liquid-liquid equilibrium (compositions of coexisting phases) at different temperatures at 308.15 K, 318.15 K and 328.15 K [51, 57, 58] and solubility at 318.15 K and 328.15 K [51, 57].

- Results of the study of critical states at 308.15 K, 318.15 K and 328.15 K [51, 57, 58] and chemically equilibrium critical compositions [59].
- Chemically equilibrium compositions for homogeneous and heterogeneous mixtures (318.15 K) [59].

Table 4. Information on the studies of the system acetic acid – n-butyl alcohol – n-butyl acetate – water in the thesis

Type of research	Temperature, K, 1 atm	Published
The system acetic acid – n-butyl alcohol – n-butyl acetate – water		
Liquid-liquid equilibrium	308.15 K	[58]
Liquid-liquid equilibrium	318.15 K	[51]
Liquid-liquid equilibrium	328.15 K	[57]
Solubility	318.15 K	[51]
Solubility	328.15 K	[57]
Critical states	308.15 K	[58]
Critical states	318.15 K	[51]
Critical states	328.15 K	[57]
Chemically Equilibrium Critical Phases	318.15 K	[59]
Chemical equilibrium	318.15 K	[59]
Ternary subsystem acetic acid – n-butyl acetate – water		
Liquid-liquid equilibrium	308.15 K	[104]
Liquid-liquid equilibrium	318.15 K	[51]
Liquid-liquid equilibrium	328.15 K	[57]
Solubility	318.15 K	[51]
Solubility	328.15 K	[57]
Critical states	308.15 K	[58]
Critical states	318.15 K	[51]
Critical states	328.15 K	[57]
Ternary subsystem acetic acid – n-butyl alcohol – water		
Liquid-liquid equilibrium	308.15 K	[58]
Liquid-liquid equilibrium	318.15 K	[51]
Liquid-liquid equilibrium	328.15 K	[57]
Solubility	318.15 K	[51]
Solubility	328.15 K	[57]
Critical states	308.15 K	[58]
Critical states	318.15 K	[51]
Critical states	328.15 K	[57]
Ternary subsystem n-butyl alcohol – n-butyl acetate – water		
Liquid-liquid equilibrium	308.15 K	[58]
Liquid-liquid equilibrium	318.15 K	[51]
Liquid-liquid equilibrium	328.15 K	[57]
Solubility	318.15 K	[51]
Solubility	328.15 K	[57]

Binary subsystem n-butyl alcohol – water		
Liquid-liquid equilibrium	308.15 K	[58]
Liquid-liquid equilibrium	318.15 K	[51]
Liquid-liquid equilibrium	328.15 K	[57]
Binary subsystem n-butyl acetate – water		
Liquid-liquid equilibrium	308.15 K	[58]
Liquid-liquid equilibrium	318.15 K	[51]
Liquid-liquid equilibrium	328.15 K	[57]

2.6.3. The system acetic acid – n-amyl alcohol – n-amyl acetate – water

The phase behavior of the acetic acid – n-amyl alcohol – n-amyl acetate – water system is similar to the previous one. The system has two binary stratified subsystems: n-amyl alcohol – water and n-amyl acetate – water. Thus, the ternary subsystems with limited solubility were n-amyl alcohol – n-amyl acetate – water, acetic acid – n-amyl alcohol – water, and acetic acid – n-amyl acetate – water (Fig. 2.6.3.1). Fig. 2.6.3.1 also shows the solubility compositions of the quaternary system and the compositions of the critical phases. Chemically equilibrium homogeneous and heterogeneous compositions were studied for three temperatures (303.15 K, 318.15 K, and 323.15 K).

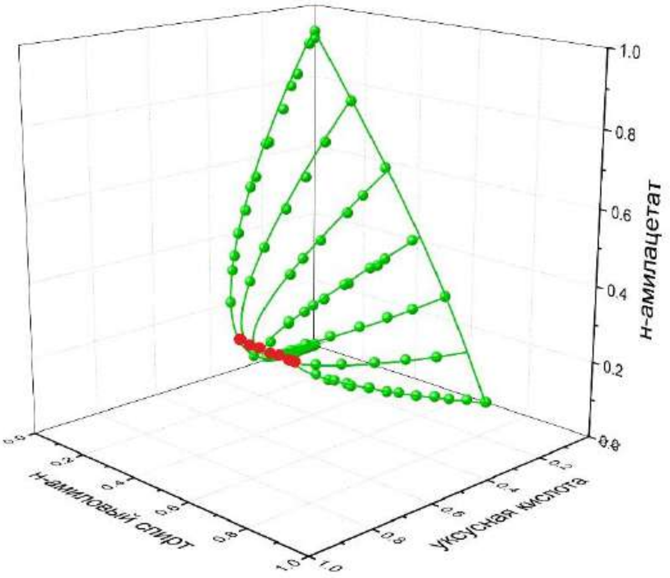

Fig. 2.6.3.1. Binodal surface (● – compositions belonging to the phase equilibrium surface [61, 62, 110]) and the critical curve formed by the critical points (●) [110], for the system acetic acid – n-amyl alcohol – n-amyl acetate – water at 303.15 K and atmospheric pressure (mole fractions).

The characteristics and scope of the studies performed are presented in Table 5. Specific data and results with reference to our published works:

- Results of the study of liquid-liquid equilibrium (compositions of coexisting phases) at different temperatures of 293.15 K, 303.15 K, 313.15 K and 323.15 K [61, 62, 110] and solubility at the same temperatures [61, 110].
- Critical compositions of liquid-liquid equilibrium phases, as well as chemically equilibrium critical points at 303.15 K and 318.15 K [63, 110].
- Chemically equilibrium compositions for homogeneous and heterogeneous mixtures at 318.15 K [63] and 323.15 K [66].

Table 5. Information on the studies of the system acetic acid – n-amyl alcohol – n-amyl acetate – water in the thesis

Type of research	Temperature, K, 1 atm	Published
The system acetic acid – n-amyl alcohol – n-amyl acetate – water		
Liquid-liquid equilibrium	293.15 K	[62]
Liquid-liquid equilibrium	303.15 K	[62, 110]
Liquid-liquid equilibrium	313.15 K	[62]
Liquid-liquid equilibrium	323.15 K	[62]
Solubility	293.15 K	[61]
Solubility	303.15 K	[61, 110]
Solubility	313.15 K	[61]
Solubility	323.15 K	[61]
Critical states	303.15 K	[110]
Critical states and chemically equilibrium critical phases	318.15 K	[63]
Chemical equilibrium	318.15 K	[63]
Chemical equilibrium	323.15 K	[66]
Ternary subsystem acetic acid – n-amyl acetate – water		
Liquid-liquid equilibrium	293.15 K	[62]
Liquid-liquid equilibrium	303.15 K	[62, 110]
Liquid-liquid equilibrium	313.15 K	[62]
Liquid-liquid equilibrium	323.15 K	[62]
Solubility	293.15 K	[61]
Solubility	303.15 K	[61, 110]
Solubility	313.15 K	[61]
Solubility	323.15 K	[61]
Critical states	303.15 K	[110]
Critical states	318.15 K	[63]
Ternary subsystem acetic acid – n-amyl alcohol – water		
Liquid-liquid equilibrium	293.15 K	[62]
Liquid-liquid equilibrium	303.15 K	[62, 110]
Liquid-liquid equilibrium	313.15 K	[62]
Liquid-liquid equilibrium	323.15 K	[62]
Solubility	293.15 K	[61]
Solubility	303.15 K	[61, 110]
Solubility	313.15 K	[61]
Solubility	323.15 K	[61]
Critical states	303.15 K	[110]
Critical states	318.15 K	[63]
Ternary subsystem n-amyl alcohol – n-amyl acetate – water		
Liquid-liquid equilibrium	293.15 K	[62]
Liquid-liquid equilibrium	303.15 K	[62, 110]
Liquid-liquid equilibrium	313.15 K	[62]

Liquid-liquid equilibrium	323.15 K	[62]
Solubility	293.15 K	[61]
Solubility	303.15 K	[61, 110]
Solubility	313.15 K	[61]
Solubility	323.15 K	[61]
Binary subsystem n-amyl alcohol – water		
Liquid-liquid equilibrium	293.15 K	[61]
Liquid-liquid equilibrium	303.15 K	[61, 110]
Liquid-liquid equilibrium	313.15 K	[61]
Liquid-liquid equilibrium	323.15 K	[61]
Binary subsystem n-amyl acetate – water		
Liquid-liquid equilibrium	293.15 K	[61]
Liquid-liquid equilibrium	303.15 K	[61, 110]
Liquid-liquid equilibrium	313.15 K	[61]
Liquid-liquid equilibrium	323.15 K	[61]

2.6.4. The system propionic acid – ethyl alcohol – ethyl propionate – water

In the system, one binary subsystem (ethyl propionate – water) is stratified. Therefore, propionic acid – ethyl propionate – water and ethyl alcohol – ethyl propionate – water were studied as ternary stratifying subsystems. In the quaternary system, the heterogeneous region of stratification is part of the volume of the tetrahedron of compositions, limited by binodal curves in the indicated ternary subsystems. The binodal surface (Fig. 2.6.4.1), on which the critical curve is located, limits this region inside the tetrahedron. The shape of the solubility surface resembles a segment of a “falling drop”, consisting of a cone and a hemisphere, adjacent to each other by their bases.

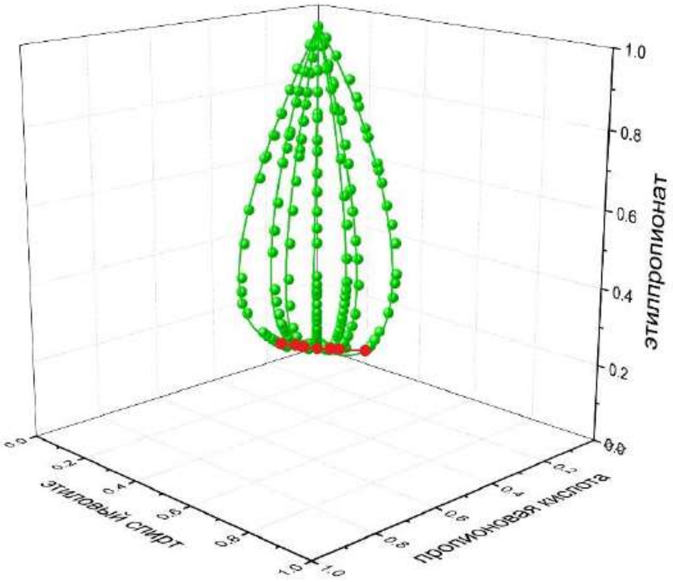

Fig. 2.6.4.1. Binodal surface (● – compositions belonging to the phase equilibrium surface [67, 76]) and the critical curve formed by the critical points (●) [67], for the system propionic acid – ethyl alcohol – ethyl propionate – water at 293.15 K and atmospheric pressure (mole fractions).

For the quaternary mixture of propionic acid – ethyl alcohol – ethyl propionate – water, the chemical equilibrium was studied at 293.15 K, 303.15 K and 313.15 K in the entire concentration range.

The characteristics and scope of the studies are given in Table 6. Specific data and results with reference to our published works:

- Results of the study of liquid-liquid equilibrium (compositions of coexisting phases) at 293.15 K and 303.15 K [76] and solubility at 293.15 K, 303.15 K and 313.15 K [67].
- Critical compositions of liquid-liquid equilibrium phases at 293.15 K, 303.15 K and 313.15 K [67].
- Chemical equilibrium compositions for homogeneous and heterogeneous mixtures at 293.15 K, 303.15 K and 313.15 K [77, 78].

Table 6. Information on the research of the propionic acid – ethyl alcohol – ethyl propionate – water system in the thesis

Type of research	Temperature, K, 1 atm	Published
The system propionic acid – ethyl alcohol – ethyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[76]
Liquid-liquid equilibrium	303.15 K	[76]
Solubility	293.15 K	[67]
Solubility	303.15 K	[67]
Solubility	313.15 K	[67]
Critical states	293.15 K	[67]
Critical states	303.15 K	[67]
Critical states	313.15 K	[67]
Chemical equilibrium	293.15 K	[78]
Chemical equilibrium	303.15 K	[77]
Chemical equilibrium	313.15 K	[77]
Ternary subsystem propionic acid – ethyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[76]
Liquid-liquid equilibrium	303.15 K	[76]
Solubility	293.15 K	[67]
Solubility	303.15 K	[67]
Solubility	313.15 K	[67]
Critical states	293.15 K	[67]
Critical states	303.15 K	[67]
Critical states	313.15 K	[67]
Ternary subsystem ethyl alcohol – ethyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[76]
Liquid-liquid equilibrium	303.15 K	[76]
Solubility	293.15 K	[67]
Solubility	303.15 K	[67]
Solubility	313.15 K	[67]
Critical states	293.15 K	[67]
Critical states	303.15 K	[67]

Critical states	313.15 K	[67]
Binary subsystem ethyl propionate - water		
Solubility	293.15 K	[67]
Solubility	303.15 K	[67]
Solubility	313.15 K	[67]

2.6.5. The system propionic acid – n-propyl alcohol – n-propyl propionate – water

By analogy with the previous system, in the mixture propionic acid – n-propyl alcohol – n-propyl propionate – water, one binary subsystem (n-propyl propionate – water) is stratified. For this system, the liquid-liquid equilibrium, solubility and critical phases had been studied (Fig. 2.6.5.1).

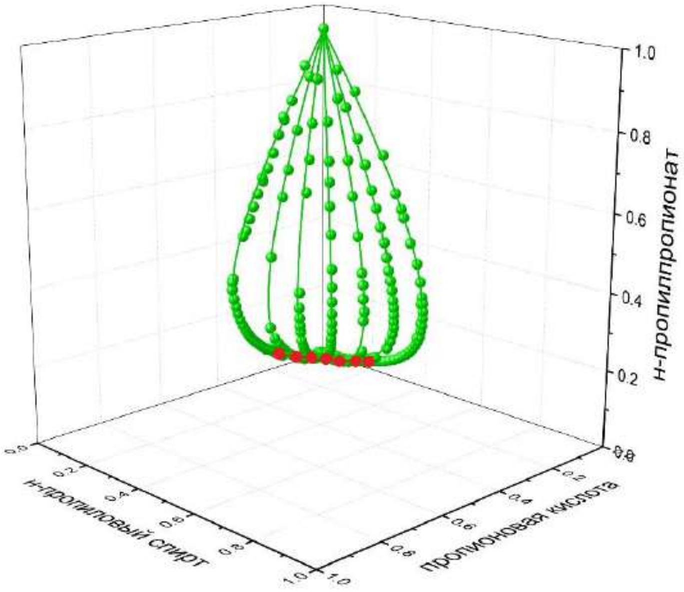

Fig. 2.6.5.1. Binodal surface (● – compositions belonging to the phase equilibrium surface [86]) and the critical curve formed by the critical points (●) [86], for the system propionic acid – n-propyl alcohol – n-propyl propionate – water at 303.15 K and atmospheric pressure (mole fractions).

The characteristics and scope of the studies conducted are presented in Table 7. Specific data and results with reference to our published works:

- Results of the study of liquid-liquid equilibrium (compositions of coexisting phases) at 293.15 K, 303.15 K, 313.15 K and 333.15 K [85, 86].
- Results of the study of solubility and critical phases at 303.15 K [86].

Table 7. Information on the studies of the propionic acid – n-propyl alcohol – n-propyl propionate – water system in the thesis

Type of research	Temperature, K, 1 atm	Published
The system propionic acid – n-propyl alcohol – n-propyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[85]
Liquid-liquid equilibrium	303.15 K	[86]
Liquid-liquid equilibrium	313.15 K	[85]
Liquid-liquid equilibrium	333.15 K	[85]
Solubility	303.15 K	[86]

Critical states	303.15 K	[86]
Ternary subsystem propionic acid – n-propyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[85]
Liquid-liquid equilibrium	303.15 K	[86]
Liquid-liquid equilibrium	313.15 K	[85]
Liquid-liquid equilibrium	333.15 K	[85]
Solubility	303.15 K	[86]
Critical states	303.15 K	[86]
Ternary subsystem n-propyl alcohol – n-propyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[85]
Liquid-liquid equilibrium	303.15 K	[86]
Liquid-liquid equilibrium	313.15 K	[85]
Liquid-liquid equilibrium	333.15 K	[85]
Solubility	303.15 K	[86]
Critical states	303.15 K	[86]
Binary subsystem n-propyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[85]
Liquid-liquid equilibrium	303.15 K	[86]
Liquid-liquid equilibrium	313.15 K	[85]
Liquid-liquid equilibrium	333.15 K	[85]

2.6.6. The system propionic acid – n-butyl alcohol – n-butyl propionate – water

With the increase of the carbon chain in alcohols, in the case of systems involving propionic acid, starting with butyl alcohol, stratification of two binary subsystems (n-butyl alcohol – water and n-butyl propionate – water) is observed. The compositions of the coexisting phases, solubility and critical states were studied (Fig. 2.6.6.1). As in the system involving n-butyl acetate and n-amyl acetate, the stratification region is a segment of an elliptical toroid.

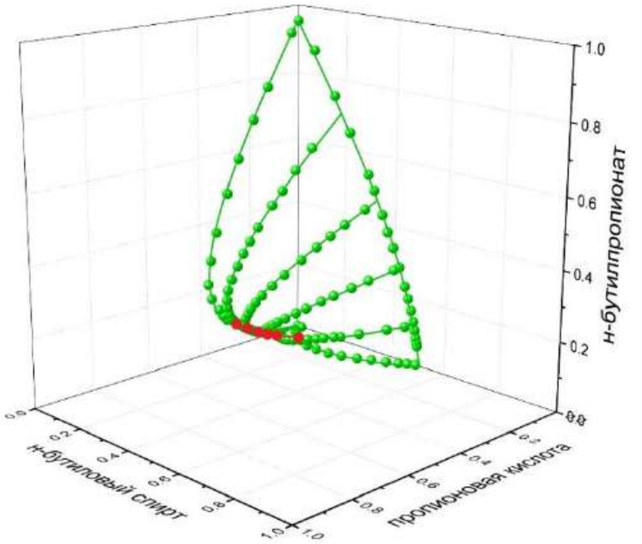

Fig. 2.6.6.1. Binodal surface (● – compositions belonging to the phase equilibrium surface [91]) and the critical curve formed by the critical points (●) [91], for the system propionic acid – n-butyl alcohol – n-butyl propionate – water at 293.15 K and atmospheric pressure (mole fractions).

The characteristics and scope of the studies conducted are presented in Table 8. Specific data and results with reference to our published works:

- Results of the study of liquid-liquid equilibrium (compositions of coexisting phases) at 293.15 K and 303.15 K [87, 91].
- Results of the study of solubility at 293.15 K [91]
- Study of the compositions of critical phases at 293.15 K and 303.15 K [87, 91].

Table 8. Information on the studies of the propionic acid – n-butyl alcohol – n-butyl propionate – water system in the thesis

Type of research	Temperature, K, 1 atm	Published
The system propionic acid – n-butyl alcohol – n-butyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[91]
Liquid-liquid equilibrium	303.15 K	[87]
Solubility	293.15 K	[91]
Critical states	293.15 K	[91]
Critical states	303.15 K	[87]
Ternary subsystem propionic acid – n-butyl alcohol – water		
Liquid-liquid equilibrium	293.15 K	[91]
Liquid-liquid equilibrium	303.15 K	[87]
Solubility	293.15 K	[91]
Critical states	293.15 K	[91]
Critical states	303.15 K	[87]
Ternary subsystem n-butyl alcohol – n-butyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[91]
Liquid-liquid equilibrium	303.15 K	[87]
Solubility	293.15 K	[91]
Ternary subsystem propionic acid – n-butyl propionate – water		
Liquid-liquid equilibrium	293.15 K	[91]
Liquid-liquid equilibrium	303.15 K	[87]
Solubility	293.15 K	[91]
Critical states	293.15 K	[91]
Critical states	303.15 K	[87]
Binary subsystem n-butyl alcohol – water		
Liquid-liquid equilibrium	293.15 K	[91]
Liquid-liquid equilibrium	303.15 K	[87]
Binary subsystem n-butyl acetate – water		
Liquid-liquid equilibrium	293.15 K	[91]
Liquid-liquid equilibrium	303.15 K	[87]

2.6.7. System oleic acid – methyl alcohol – methyl oleate – water

As a number of experiments have shown, the system with oleic acid, unlike all other mixtures studied in the thesis, has a relatively small region of homogeneous compositions in the entire range of concentrations at a given temperature and atmospheric pressure (303.15 K). The nature of such phase behavior of the system is associated with the presence of two binary subsystems, the components of which have a fairly low solubility in each other: methyl oleate – water and oleic acid – water (Fig. 2.6.7.1). It should be noted that, unlike all the systems studied in the thesis (all acids dissolve in water), only oleic acid is an exception (limited solubility). Fig. 2.6.7.1 shows the results of the study of solubility and critical phases in the oleic acid – methyl alcohol – methyl oleate – water system at 303.15 K and atmospheric pressure [92].

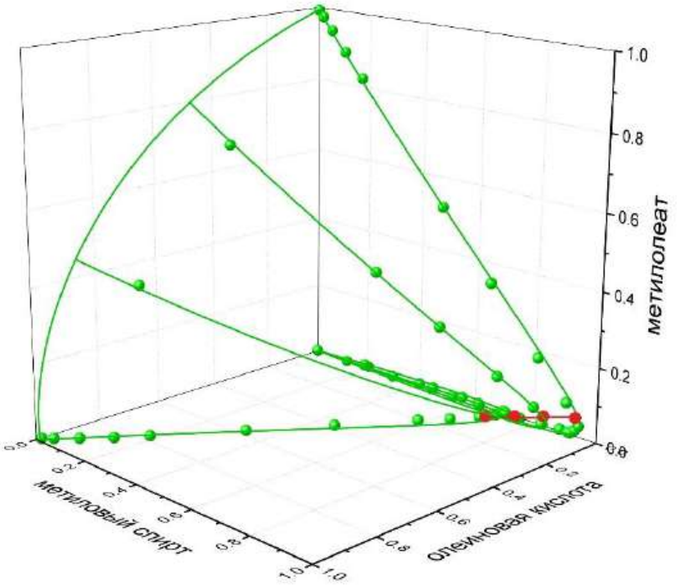

Fig. 2.6.7.1. Binodal surface (● – compositions belonging to the solubility surface [92]) and the critical curve formed by the critical points (●) [92], for the system oleic acid – methyl alcohol – methyl oleate – water at 303.15 K and atmospheric pressure (mole fractions).

The characteristics and scope of the studies conducted are given in Table 9. Specific data and results with reference to our published works:

- Results of the study of liquid-liquid equilibrium, solubility and critical compositions at 303.15 K [92]

Table 9. Information on the studies of the oleic acid – methyl alcohol – methyl oleate – water system in the thesis

Type of research	Temperature, K, 1 atm	Published
System oleic acid – methyl alcohol – methyl oleate – water		
Solubility	303.15 K	[92]
Critical states	303.15 K	[92]
Ternary subsystem oleic acid – methyl oleate – water		
Liquid-liquid equilibrium	303.15 K	[92]
Ternary subsystem methyl alcohol – methyl oleate – water		
Liquid-liquid equilibrium	303.15 K	[92]
Solubility	303.15 K	[92]
Critical states	303.15 K	[92]
Ternary subsystem oleic acid – methyl alcohol – water		
Liquid-liquid equilibrium	303.15 K	[92]
Solubility	303.15 K	[92]

Critical states	303.15 K	[92]
Binary subsystem methyl oleate – water		
Liquid-liquid equilibrium	303.15 K	[92]
Binary subsystem oleic acid – water		
Liquid-liquid equilibrium	303.15 K	[92]

CHAPTER 3. STATE DIAGRAMS STRUCTURES AND THERMODYNAMIC FEATURES OF MULTI-COMPONENT LIQUID–LIQUID SYSTEMS WITH CHEMICAL REACTIONS AND CRITICAL PHASES

The experimental results presented in the previous chapter, to the best of our knowledge, had no direct analogues in the world literature either at the time of their publication (since 2006) or, for the most part, at the present time. This is due to the peculiarities of the experimental studies, the data obtained, and, accordingly, the specific nature of the goals and objects of the work: multicomponent fluid systems with critical regions, chemically equilibrium critical phases, and critical surfaces. Note that a number of works in recent decades included consideration of chemical reactions in the vicinity of a critical state [111–117] or critical surfaces [118], but these publications mainly included theoretical and computational consideration of the indicated features. A number of earlier works, for example, [119–121], were related to experimental studies of kinetics in the vicinity of a critical state, but, apparently, these works did not receive further development in theoretical and experimental terms. Let us first recall some of the main provisions in the context of the objectives of the present study. Next, we present new results, including an additional discussion of the experimental data.

3.1. On the general thermodynamic conditions that determine the features of the structures of state diagrams of systems with chemical interaction and critical phases

According to the phase rule, the number of degrees of freedom f in systems with k equilibrium chemical reactions is determined by the following equation [122-127]:

$$f = n + 2 - r - k \qquad (3.1.1)$$

where n and r are the numbers of substances and phases. Accordingly, a binary two-phase system without chemical reactions (or a chemically nonequilibrium system) has two degrees of freedom. At variable temperature and pressure, its states are represented as a surface in the three-dimensional thermodynamic space “composition-temperature-pressure”. A homogeneous binary system with one equilibrium chemical reaction (i.e. in a state of chemical equilibrium) also has two degrees of freedom. In the three-dimensional thermodynamic space “composition-temperature-pressure”, chemical equilibrium in such a system can be represented as a surface. For simultaneous phase and chemical equilibrium in a binary two-phase system

$$f = n + 2 - r - k = 2 + 2 - 2 - 1 = 1 \qquad (3.1.2)$$

Accordingly, such a combined equilibrium is represented as a curve in the three-dimensional thermodynamic space “composition – temperature – pressure”. In a system of four substances with variables T and P, the states of chemical equilibrium belong to a hypersurface in the five-dimensional thermodynamic space “composition-temperature-pressure”, and a visual graphical representation is impossible. The restriction $T,P = const$ (isothermal-isobaric conditions) reduces the number of degrees of freedom

$$f = n + 2 - r - k = 4 + 2 - 1 - 1 - 2 \qquad (3.1.3)$$

and the chemical equilibrium can be represented as a surface in a compositional tetrahedron. The same result $f = 2$ is valid for a two-phase equilibrium in a quaternary system without reactions or in the case of a nonequilibrium chemical reaction: the binodal must also be represented as a surface in a tetrahedron. Recall that, according to the phase rule, the variance of systems in chemically nonequilibrium states is the same as in the case of systems without reactions.

The variance of a quaternary two-phase mixture in simultaneous phase (the case of two phases) and chemical equilibrium under isothermal-isobaric conditions is determined as follows:

$$f = n + 2 - r - k = 4 + 2 - 2 - 1 - 2 = 1, \qquad (3.1.4)$$

that is, such an equilibrium should be represented as a curve in a concentration tetrahedron.

It is obvious that the variety of thermodynamically possible types of diagrams of systems with similar combined equilibria for both ternary and quaternary systems is extremely large. Some types of diagrams have been discussed by us earlier [12, 38, 43, 48]. Therefore, here and below we, as a rule, limit the discussion to some practically important types of diagrams.

Critical states of two-phase equilibrium in binary fluid systems are usually considered as a critical point on the “composition-temperature” diagrams. In ternary stratified systems, liquid-liquid critical points are realized for some types of diagrams: systems with a heterogeneous region in the form of a “strip”, as a rule, do not have critical points. At a variable temperature, the set of critical points forms a critical curve in the concentration triangle. In quaternary systems under isothermal-isobaric conditions, critical states of two-phase equilibrium can be represented as a curve in the concentration tetrahedron (a set of critical points on the binodal surface). In the general case of multicomponent liquid-liquid systems, critical states correspond to different manifolds (points, curves, surfaces or hypersurfaces) in a multidimensional thermodynamic space.

Gibbs proposed conditions for a critical condition ("critical phases" [122] Gibbs, p. 129-134) as the following relations:

$$\left(\frac{\partial \mu_n}{\partial m_n}\right)_{T,V,\mu_1,\mu_2,\dots\,\mu_{n-1}} = 0, \qquad (3.1.5)$$

$$\left(\frac{\partial^2 \mu_n}{\partial {m_n}^2}\right)_{T,V,\mu_1,\mu_2,\dots\,\mu_{n-1}} = 0, \qquad (3.1.6)$$

$$\left(\frac{\partial^3 \mu_n}{\partial {m_n}^3}\right)_{T,V,\mu_1,\mu_2,\dots\,\mu_{n-1}} \geq 0, \qquad (3.1.7)$$

The first two relations, (3.1.5) and (3.1.6), are the equations of the critical point (phase, state). Relation (3.1.7) is the condition of its stability: if it is satisfied with the equality sign, then infinitesimals of higher orders must be taken into account. Further in [122] matrix forms of recording the conditions of the critical state were also considered. In the subsequent text, considering these general conditions, we will use the term "critical phases" in accordance with the terminology of Gibbs [122], as well as in the books [127, 128].

Due to the conditions of the critical state, the number of degrees of freedom decreases: the critical phase (when counting according to the phase rule) should be taken into account three times [122, 127, 128]. For example, the critical phase in a quaternary two-phase system in a state of simultaneous phase and chemical equilibrium at constant temperature (T) and pressure (P) is in a nonvariant state:

$$f = n + 2 - r - k = 4 + 2 - 3 - 1 - 2 = 0 \qquad (3.1.8)$$

At variable T, these states correspond to the curve in the composition tetrahedron. In the absence of chemical reactions (chemical equilibrium), the critical states of the quaternary system (or the system in chemically nonequilibrium states) at constant T and P correspond to the curve in the concentration tetrahedron (monovariant state). At variable T, the number of degrees of freedom is 2

$$f = n + 2 - r - k = 4 + 2 - 3 - 0 - 1 = 2 \quad (3.1.9)$$

and these states correspond to the critical surface in the concentration tetrahedron.

It is obvious that thermodynamic analysis of the behavior of multicomponent critical phases is a non-standard task, despite certain achievements in this area (see, for example, [33, 43, 45, 111, 128, 129]). Even greater difficulties arise in the case of systems with chemical interaction of substances. In the next paragraph, a possible approach to some aspects of the study of critical states of chemically reacting systems will be presented.

3.2. Diagonalization of the stability matrix and transformation of critical state conditions for ternary chemically reacting systems

In this section, we consider one of the options for representing the properties of critical phases in systems with chemical reactions by introducing new concentration variables (different from α-variables), which make it possible to reduce the number of independent variables and transform the stability matrix to a diagonal form. We will consider the case of only ternary systems, since generalizations to systems of four substances unfortunately lead to extremely cumbersome relationships. Here, this approach proposed by us is given as an illustration of possible, previously considered, options for analyzing systems with critical phases and chemical interactions.

In variables T, P, m_1, m_2,…m_n, (where m_i – amount of substance i) the critical phase equations are conveniently written in matrix form [122]. We will restrict ourselves, as already indicated, to the case of a system of three substances and present the critical phase equations in matrix form for the variables T, P, x_1, x_2,…x_n (where x_i – amount of substance i). At T, $P = const$ the first equation of the critical phase is [127, 128]:

$$D \equiv \begin{vmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{vmatrix} = 0, \quad (3.2.1)$$

where g_{ij} – second derivatives of the molar Gibbs energy g with respect to the corresponding mole fractions of substances:

$$g_{ij} = \frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_n}{\partial x_j}. \quad (3.2.2)$$

The second equation of the critical phase in this case has the form:

$$\begin{vmatrix} \frac{\partial D}{\partial x_1} & \frac{\partial D}{\partial x_2} \\ g_{21} & g_{22} \end{vmatrix} = 0 \text{ или } \begin{vmatrix} g_{11} & g_{12} \\ \frac{\partial D}{\partial x_1} & \frac{\partial D}{\partial x_2} \end{vmatrix} = 0. \quad (3.2.3)$$

Let now an equilibrium chemical reaction (chemical equilibrium) take place in the system:

$$\sum_{i=1}^{3} \nu_i R_i = 0, \quad (3.2.4)$$

where R_i – substance symbol i, ν_i – its stoichiometric coefficient in reaction (3.2.4). The stoichiometric coefficients for the reaction products, as usual, are taken to be positive, and for the starting materials, negative. Chemical equilibrium is satisfied by the condition

$$\sum_{i=1}^{3} \nu_i \mu_i = 0, \quad (3.2.5)$$

and its displacement is the equation

$$\sum_{i=1}^{3} \nu_i d\mu_i = 0, \quad (3.2.6)$$

Thus, the problem of chemical equilibrium in a critical state or of the shift of the said equilibrium is reduced to a joint consideration of the critical phase equations (3.2.1) and (3.2.3) and the chemical equilibrium condition (3.2.5) (or (3.2.6)). However, their direct unification leads to rather cumbersome relations, the analysis of which is difficult. Therefore, to solve the problem, we use the method proposed in [130-133], which consists of transforming the stability matrix to a diagonal form, and the corresponding representation of the critical phase equations.

Let's introduce new variables $\widetilde{m_i}$, defined by the following relationship:

$$\tilde{m}_i = \sum_{j=1}^{n} c_{ji} m_j, \tag{3.2.7}$$

where c_{ji} – some real coefficients. Let us conventionally call these variables "generalized numbers of moles". In matrix notation (3.2.7) has the form:

$$\tilde{m} = cm, \tag{3.2.8}$$

where $\tilde{m}$ и m – column vectors of generalized and ordinary mole numbers, respectively. With respect to the linear transformation matrix $\|c_{ij}\|$ we will assume only that it is orthogonal. In accordance with (3.2.7), the analogs of mole fractions $\widetilde{x_i}$ are determined by the ratio:

$$\widetilde{x_i} = \frac{\tilde{m}_i}{\sum \tilde{m}_i} \quad . \tag{3.2.9}$$

As with conventional mole fractions, for $\tilde{x}_i$ the condition is satisfied $\sum_{i=1}^{n} \tilde{x}_i = 1$. Moreover, it is obvious that the linear transformation $m_i \to \tilde{m}_i$ coincides with a linear transformation $x_i \to \tilde{x}_i$:

$$\tilde{x}_i = \sum_{j=1}^{n} c_{ji} x_j, \tag{3.2.10}$$

which can be easily verified by taking the total number of generalized moles as unity:

$$\sum_{i=1}^{n} \tilde{m}_i = 1.$$

Let us introduce “generalized chemical potentials” $\tilde{\mu}_i$, having determined them from the ratio

$$dG = -SdT + VdP + \sum_{i=1}^{n} \tilde{\mu}_i d\tilde{m}_i \tag{3.2.11}$$

(S and G – respectively, entropy and Gibbs energy), that is:

$$\tilde{\mu}_i = \left(\frac{\partial G}{\partial \tilde{m}_i}\right)_{P,T} \tag{3.2.12}$$

The relationship between chemical potentials and quantities $\tilde{\mu}_i$ can be easily established based on relations (3.2.7) and (3.2.12):

$$\mu_i = \frac{\partial G}{\partial m_i} = \sum_{j=1}^{n} \frac{\partial G}{\partial \tilde{m}_j} \frac{\partial \tilde{m}_j}{\partial m_i} = \sum_{j=1}^{n} \tilde{\mu}_j c_{ij}, \tag{3.2.13}$$

Note that due to the linear nature of the transformation corresponding to relation (3.2.7), the Gibbs energy remains a homogeneous function of the first degree with respect to the generalized numbers of moles $\tilde{m}_j$ and can be represented in the following integral form:

$$G = \sum_{i=1}^{n} \tilde{m}_i \tilde{\mu}_i, \tag{3.2.14}$$

and for the molar Gibbs energy it is true:

$$g = \sum_{i=1}^{n} \tilde{x}_i \tilde{\mu}_i. \tag{3.2.15}$$

From (3.2.11) and (3.2.14) for isothermal-isobaric conditions follows the equation

$$\sum_{i=1}^{n} \tilde{m}_i d\tilde{\mu}_i = 0 \tag{3.2.16}$$

– the result of Legendre transformations, which is an analogue of the Gibbs-Duhem equation for T, $P = const$. For partial derivatives the following equalities will be satisfied:

$$\sum_{i=1}^{n} \tilde{m}_i \left(\frac{\partial \tilde{\mu}_i}{\partial \tilde{m}_j}\right) = 0 \tag{3.2.17}$$

or, taking into account the reciprocity relations:

$$\sum_{i=1}^{n} \tilde{m}_i \left(\frac{\partial \tilde{\mu}_j}{\partial \tilde{m}_i}\right) = 0. \tag{3.2.18}$$

These same relationships can be written in terms of generalized mole fractions of substances:

$$\sum_{i=1}^{n}\tilde{x}_i\frac{\partial\tilde{\mu}_i}{\partial\tilde{x}_j}=0, \qquad (3.2.19)$$

$$\sum_{i=1}^{n}\tilde{x}_i\frac{\partial\tilde{\mu}_j}{\partial\tilde{x}_i}=0. \qquad (3.2.20)$$

Relation (3.2.19) corresponds to a change in state with constant numbers of generalized moles of all substances except substance *j*, and relation (3.2.20) connects the partial derivatives of the chemical potential of a given substance (*j*) with respect to the generalized moles of all substances. These relations are also analogous to the partial forms of the Gibbs-Duhem equation with *T*, *P* = *const* [124].

Differentiation of *g* with respect to independent variables of the composition $\tilde{x}_i$ (*i* = 1, 2,…n-1) leads to the ratio

$$\frac{\partial g}{\partial\tilde{x}_i}=\tilde{\mu}_i-\tilde{\mu}_n. \qquad (3.2.21)$$

For these partial derivatives we introduce notations similar to (3.2.2):

$$\tilde{g}_{ii}=\frac{\partial\tilde{\mu}_i}{\partial\tilde{x}_i}-\frac{\partial\tilde{\mu}_n}{\partial\tilde{x}_i} \text{ и } \tilde{g}_{ij}=\tilde{g}_{ji}=\frac{\partial\tilde{\mu}_i}{\partial\tilde{x}_j}-\frac{\partial\tilde{\mu}_n}{\partial\tilde{x}_j}=\frac{\partial\tilde{\mu}_j}{\partial\tilde{x}_i}-\frac{\partial\tilde{\mu}_n}{\partial\tilde{x}_i} \qquad (3.2.22)$$

The nature of the linear transformation (3.2.7) makes it possible to write down the stability conditions [122] directly in terms of derivatives of the generalized mole fractions $\tilde{x}_i$. In the case of a system of three substances we obtain:

$$\begin{vmatrix}\tilde{g}_{11} & \tilde{g}_{12}\\ \tilde{g}_{21} & \tilde{g}_{22}\end{vmatrix}\geq 0,\ \tilde{g}_{11}\geq 0,\ \tilde{g}_{22}\geq 0. \qquad (3.2.23)$$

Accordingly, the first equation of the critical phase (3.2.1) takes the form:

$$\tilde{D}=\begin{vmatrix}\tilde{g}_{11} & \tilde{g}_{12}\\ \tilde{g}_{21} & \tilde{g}_{22}\end{vmatrix}=0. \qquad (3.2.24)$$

Now we transform the condition of chemical equilibrium in terms of generalized mole fractions

$$\sum_{i=1}^{n}\nu_i\mu_i=0, \qquad (3.2.25)$$

having written it down taking into account (3.2.13) as follows:

$$\sum_{i=1}^{n}\nu_i\sum_{j=1}^{n}\tilde{\mu}_j\,c_{ij}=\sum_{j=1}^{n}\tilde{\mu}_j\sum_{i=1}^{n}\nu_i\,c_{ij}=0. \qquad (3.2.26)$$

Let us introduce the notation: $\tilde{\nu}_j\equiv\sum_{i=1}^{n}\nu_i c_{ij}$. Then the condition of chemical equilibrium (3.2.26) takes the form

$$\sum_{j=1}^{n}\tilde{\nu}_j\tilde{\mu}_j=0, \qquad (3.2.27)$$

coinciding with the conditions of chemical equilibrium in ordinary variables.

For a better illustration of the results, we will again restrict ourselves to chemical reactions in systems of three substances (ternary systems) with separation of the liquid phase. In the general case, chemical equilibrium in such systems at a given temperature and pressure corresponds to a curve in the concentration triangle connecting the points of the compositions of two pure reactants, i.e., two vertices of the triangle. In the separation region, the chemical equilibrium curve coincides with the so-called unique reactive tie-line [37, 38, 43, 103, 134]. When external parameters (e.g., temperature) change, this tie-line can shift to the critical point. In this case, a joint chemical equilibrium and a critical state are realized. The previously proposed brief preliminary classification of such diagrams covers mainly systems that are common in practice [38, 135]. General theoretical thermodynamic analysis was not carried out. Let us consider a number of features of the behavior of ternary liquid-liquid systems with chemical interaction of substances in the vicinity of a critical state, based on the above relations.

When the chemical equilibrium of reaction (3.2.4) is shifted

$\nu_1 R_1 + \nu_2 R_2 + \nu_3 R_3 = 0.$

from (3.2.27) follows the obvious condition:

$$\sum_{i=1}^{3} \tilde{\nu}_i \tilde{\mu}_i = 0. \qquad (3.2.28)$$

For a joint solution of this equation and the critical phase equation, it is convenient to express condition (3.2.28) in terms of the quantities $\tilde{g}_{ij}$. Let's represent the quantities $\tilde{\mu}_i$ as functions of independent variables $\tilde{x}_1$ and $\tilde{x}_2$ (at *T*, *P* = *const*):

$$d\tilde{\mu}_i = \frac{\partial \tilde{\mu}_i}{\partial \tilde{x}_1} d\tilde{x}_1 + \frac{\partial \tilde{\mu}_i}{\partial \tilde{x}_2} d\tilde{x}_2. \qquad (3.2.29)$$

Then equation (3.2.28) takes the form

$$\left(\tilde{\nu}_1 \frac{\partial \tilde{\mu}_1}{\partial \tilde{x}_1} + \tilde{\nu}_2 \frac{\partial \tilde{\mu}_2}{\partial \tilde{x}_1} + \tilde{\nu}_3 \frac{\partial \tilde{\mu}_3}{\partial \tilde{x}_1}\right) d\tilde{x}_1 + \left(\tilde{\nu}_1 \frac{\partial \tilde{\mu}_1}{\partial \tilde{x}_2} + \tilde{\nu}_2 \frac{\partial \tilde{\mu}_2}{\partial \tilde{x}_2} + \tilde{\nu}_3 \frac{\partial \tilde{\mu}_3}{\partial \tilde{x}_2}\right) d\tilde{x}_2 = 0$$

Expressing from (3.2.29) the quantities $\frac{\partial \tilde{\mu}_i}{\partial \tilde{x}_j}$ and substituting them into equation (3.2.22), we obtain:

$$\frac{\partial \tilde{\mu}_j}{\partial \tilde{x}_j} = (1 - \tilde{x}_j)\tilde{g}_{jj} - \sum_{i \neq j}^{n-1} \tilde{x}_i \tilde{g}_{ij}, \qquad j = 1, 2, \dots (n-1). \qquad (3.2.30)$$

$$\frac{\partial \tilde{\mu}_i}{\partial \tilde{x}_j} = \tilde{g}_{ij} - \sum_{k=1}^{n-1} \tilde{x}_k \tilde{g}_{kj}, \qquad (3.2.31)$$

$$\frac{\partial \tilde{\mu}_n}{\partial \tilde{x}_j} = -\sum_{k=1}^{n-1} \tilde{x}_k \tilde{g}_{kj}. \qquad (3.2.32)$$

Using equations (3.2.30) – (3.2.32), we obtain from (3.2.29):

$$[\tilde{g}_{11}(\tilde{\nu}_1 - \tilde{x}_1 \Delta\tilde{\nu}) + \tilde{g}_{12}(\tilde{\nu}_2 - \tilde{x}_2 \Delta\tilde{\nu})] d\tilde{x}_1 + [\tilde{g}_{22}(\tilde{\nu}_2 - \tilde{x}_2 \Delta\tilde{\nu}) + \tilde{g}_{12}(\tilde{\nu}_1 - \tilde{x}_1 \Delta\tilde{\nu})] d\tilde{x}_2 =$$
$$= 0 \qquad (3.2.33)$$

where $\Delta\tilde{\nu} = \sum_{i=1}^{3} \tilde{\nu}_i$. Note that when the numbers of moles are maintained during the reaction (that is, when $\sum_{i=1}^{3} \nu_i = 0$) sum $\sum_{i=1}^{3} \tilde{\nu}_i$, unlike the usual stoichiometric coefficients, is not necessarily equal to zero. Equation (3.2.33) is the equation of the isothermal-isobaric curve of chemical equilibrium of a ternary reaction system in generalized concentration variables.

Obviously, for the differential of internal energy in these variables, the following is also true

$$dU = TdS - PdV + \sum_{i=1}^{n} \tilde{\mu}_i d\tilde{m}_i \ . \qquad (3.2.34)$$

Consequently, when writing the fundamental equations in variables m˜_i, the conditions of thermal and mechanical equilibria, as expected, have the usual form, and the condition of equilibrium with respect to diffusion is satisfied in terms of generalized chemical potentials $\tilde{\mu}_i$.

We apply condition (3.2.23) to analyze the behavior of chemically reacting systems in the vicinity of critical points of two-phase liquid-liquid equilibria. We define the character of the linear orthogonal transformation (3.2.7) in such a way that it reduces the real symmetric matrix $\left\|\frac{\partial^2 g}{\partial x_i \partial x_j}\right\| \equiv \|\tilde{g}_{ij}\|$ to the diagonal form. This, according to [136], is always possible. Let us expand the functions $\tilde{g}_{ij}$ in a row in the vicinity of the critical point. The quantities related to the critical state will be designated by the superscript “o”. Then, due to the diagonality of the matrix $\|\tilde{g}_{ij}\|$ ($\tilde{g}_{ij} = 0$ at $i \neq j$), we will get

$$\tilde{g}_{11} = \tilde{g}_{11}^{o} + \tilde{g}_{111}^{o} d\tilde{x}_1 + \tilde{g}_{112}^{o} d\tilde{x}_2 + \frac{1}{2}(\tilde{g}_{1111}^{o} d\tilde{x}_1^2 + 2\tilde{g}_{1112}^{o} d\tilde{x}_1 d\tilde{x}_2 + \tilde{g}_{1122}^{o} d\tilde{x}_2^2) + \cdots, \qquad (3.2.35)$$

$$\tilde{g}_{12} = \tilde{g}_{112}^{o} d\tilde{x}_1 + \tilde{g}_{122}^{o} d\tilde{x}_2 + \frac{1}{2}(\tilde{g}_{1112}^{o} d\tilde{x}_1^2 + 2\tilde{g}_{1122}^{o} d\tilde{x}_1 d\tilde{x}_2 + \tilde{g}_{1222}^{o} d\tilde{x}_2^2) + \cdots, \qquad (3.2.36)$$

$$\tilde{g}_{22} = \tilde{g}_{22}^{o} + \tilde{g}_{122}^{o} d\tilde{x}_1 + \tilde{g}_{222}^{o} d\tilde{x}_2 + \frac{1}{2}(\tilde{g}_{1122}^{o} d\tilde{x}_1^2 + 2\tilde{g}_{1222}^{o} d\tilde{x}_1 d\tilde{x}_2 + \tilde{g}_{2222}^{o} d\tilde{x}_2^2) + \cdots, \quad (3.2.37)$$

where $\tilde{g}_{ijk}$ and $\tilde{g}_{ijkl}$ – first and second derivatives of quantities $\tilde{g}_{ij}$ with respect to $\tilde{x}_k$ and $\tilde{x}_l$ $(k, l = 1, 2)$. For the critical phase, the determinant in (3.2.23) has a zero value. Thus, as a result of diagonalizing the stability matrix $\|\tilde{g}_{ij}\|$ the critical phase equations take the form:

$$\begin{vmatrix} \tilde{g}_{11}^{o} & 0 \\ 0 & \tilde{g}_{22}^{o} \end{vmatrix} = 0, \ \tilde{g}_{11}^{o} \geq 0, \ \tilde{g}_{22}^{o} \geq 0. \quad (3.2.38)$$

As follows from (3.2.38), at the critical point the diagonal matrix $\|\tilde{g}_{ij}\|$ must be degenerate. Let us first consider the case of a single degeneracy of the stability matrix, when one of the quantities – $\tilde{g}_{11}^{o}$ or $\tilde{g}_{22}^{o}$ – takes on a zero value. Both variants are identical, so it is sufficient to consider the case

$$\tilde{g}_{11}^{o} = 0, \qquad \tilde{g}_{22}^{o} > 0. \quad (3.2.39)$$

Then, as was shown in [128, 132],

$\tilde{g}_{111}^{o} = 0$. Therefore, substituting (3.2.35) – (3.2.37) into (3.2.33) we obtain, up to infinitesimals of the first order:

$$\tilde{g}_{22}^{o}(\tilde{v}_2 - \tilde{x}_2^{o}\Delta\tilde{v})d\tilde{x}_2 = 0. \quad (3.2.40)$$

Since $\tilde{g}_{22}^{o} > 0$ and, in general, $\tilde{v}_2 - \tilde{x}_2^{o}\Delta\tilde{v} \neq 0$, then, therefore:

$$d\tilde{x}_2 = 0. \quad (3.2.41)$$

The last equality means that in the case of a single degeneration of the stability matrix, the tangent to the chemical equilibrium curve in the vicinity of the critical point is parallel to the coordinate axis $O\tilde{x}_1$. We will assume that the critical point is at the origin of coordinates: this can be achieved by parallel translation of the coordinate axes, which does not limit the generality of the above and further conclusions. It is obvious that then the tangent to the chemical equilibrium curve in the vicinity of the critical point simply coincides with the coordinate axis $O\tilde{x}_1$. In works [130-133] the forms of binodals of two-phase equilibria were determined for single and complete degenerations of the stability matrix in the vicinity of critical points. We use these results to analyze the behavior of the chemical equilibrium curve [137]. Variants for the case of single degeneration of the stability matrix are presented in Fig. 3.2.1. Since a small vicinity of the critical point is considered, it is sufficient to consider the location of the tangents to the desired curves (chemical equilibrium and binodal).

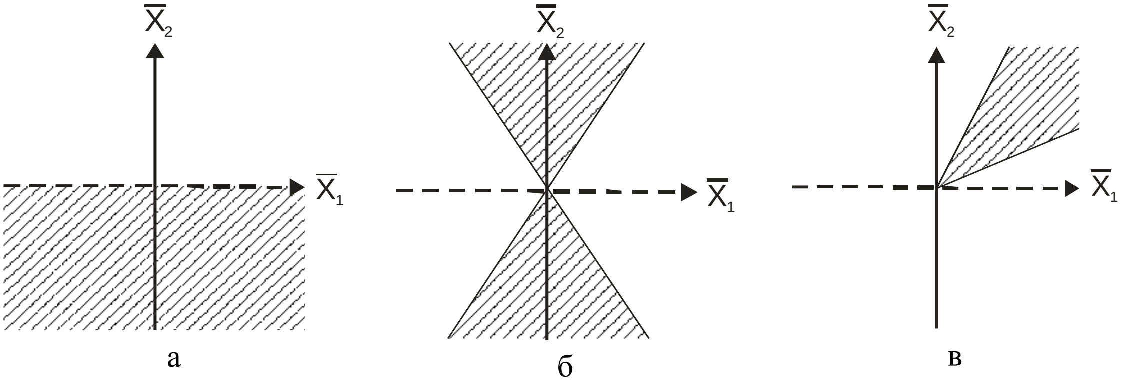

Fig. 3.2.1. Schematic representation of the chemical equilibrium curve in a ternary system with a chemical reaction (single degeneration of the stability matrix) in the vicinity of the critical point. The heterogeneous region is shaded. Tangents to the binodal (solid lines) and to the chemical equilibrium curve (dashed lines) are shown.

It is obvious that only the type of binodal in Fig. 3.2.1a corresponds to their usual arrangement – “smooth binodal” [130, 133]. The arrangement of binodals in Fig. 3.2.1b (two regions with a break point) and in Fig. 3.2.1c (region with a return point) is theoretically possible [130, 133], but only in the case of a smooth binodal does the binodal touch the chemical equilibrium curve.

Let us consider the case of complete degeneration of the stability matrix. In this case $\tilde{g}^o_{11} = \tilde{g}^o_{22} = 0$ and, as shown in [131], $\tilde{g}^o_{ijk} = 0\ (i, j, k = 1{,}2)$. Then, after substituting expressions (3.2.35) – (3.2.37) into equation (3.2.33), taking into account the third-order infinitesimals, we obtain

$$(\tilde{g}^o_{1111}\alpha_1 + \tilde{g}^o_{1112}\alpha_2)d\tilde{x}_1^3 + 3(\tilde{g}^o_{1112}\alpha_1 + \tilde{g}^o_{1122}\alpha_2)d\tilde{x}_1^2 d\tilde{x}_2 + 3(\tilde{g}^o_{1122}\alpha_1 + \\ +\tilde{g}^o_{1222}\alpha_2)d\tilde{x}_1 d\tilde{x}_2^2 + (\tilde{g}^o_{1222}\alpha_1 + \tilde{g}^o_{2222}\alpha_2)d\tilde{x}_2^3 = 0, \qquad (3.2.42)$$

where $\alpha_1 \equiv \tilde{v}_1 - \tilde{x}_1^o\Delta\tilde{v}$, $\alpha_2 \equiv \tilde{v}_2 - \tilde{x}_2^o\Delta\tilde{v}$. Equation (3.2.42) can be reduced to a cubic equation with respect to $\frac{d\tilde{x}_2}{d\tilde{x}_1}$, that is, the value that determines the position of the tangent to the chemical equilibrium curve at the critical point:

$$(\tilde{g}^o_{1222}\alpha_1 + \tilde{g}^o_{2222}\alpha_2)\left(\frac{d\tilde{x}_2}{d\tilde{x}_1}\right)^3 + 3(\tilde{g}^o_{1122}\alpha_1 + \tilde{g}^o_{1222}\alpha_2)\left(\frac{d\tilde{x}_2}{d\tilde{x}_1}\right)^2 + \\ +3(\tilde{g}^o_{1112}\alpha_1 + \tilde{g}^o_{1122}\alpha_2)\frac{d\tilde{x}_2}{d\tilde{x}_1} + \tilde{v}_1\tilde{g}^o_{1111}\alpha_1 + \tilde{v}_2\tilde{g}^o_{1112}\alpha_2 = 0. \qquad (3.2.43)$$

Since the cubic equation has either one or three real roots, then, in the case of complete degeneration of the stability matrix, a wide variety of mutual arrangements of the chemical equilibrium curve and binodal curves in the immediate vicinity of the critical point is possible. Variants of the course of binodals in the case of complete degeneration of the stability matrix are considered in [131]. The distribution of real roots of equation (3.2.43) can be represented as follows:

1) One real root, or a root of multiplicity three.
2) Two different roots, one of which has multiplicity two.
3) The equation has three different real roots.

From a physical point of view, cases 1–3 correspond to the presence of one, two or three branches of the chemical equilibrium curve that have different directions near the critical point. In other words, the chemical equilibrium curve undergoes a break at the critical point and even “branching”. Fig. 3.2.2 shows examples of two variants of contact between the chemical equilibrium curve and binodals

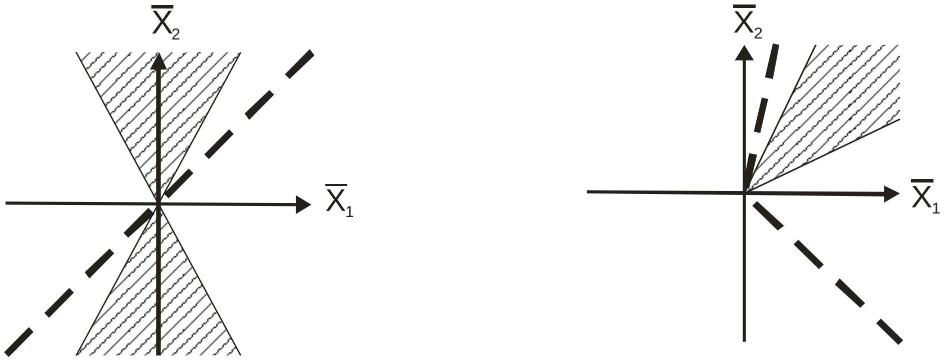

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Fig. 3.2.2. Possible cases of contact between the chemical equilibrium curve and binodals in the vicinity of the critical point in the case of complete degeneration of the stability matrix. a – one branch of the chemical equilibrium curve (no break), b – two branches (break). The designations are the same as in Fig. 3.2.1.

Note that the variants of single and complete degeneration of the stability matrix have a qualitative difference: if in the case of single degeneration the chemical equilibrium curve and the binodal can touch each other (one of the possible variants, Fig. 3.2.1a), then in the case of complete degeneration the touch no longer takes place, and the coefficients of the resulting cubic equation, and, consequently, its roots, depend not only on the quantities determined by the position of the critical point ($\tilde{g}^{o}_{ijkl}$), but also from $\tilde{\nu}_1$ and $\tilde{\nu}_2$, i.e. from the parameters characterizing the chemical reaction itself.

The variant of thermodynamic analysis of phase diagrams of multicomponent liquid-liquid systems with chemical interaction of substances and critical phases presented in this section is illustrated by the example of ternary systems for which experimental information is limited; only theoretical works are presented in the literature [38, 43, 103, 134, 135]. In the case of systems with a large number of components, reducing the stability matrix to a diagonal form with the introduction of the corresponding modified concentration variables does not encounter formal difficulties. At the same time, as already indicated, the final relations turn out to be quite cumbersome for application to specific experimental data. Therefore, the results of this section are not discussed further. Nevertheless, the presented approach, with additional modification, can be a promising basis for thermodynamic analysis of critical phenomena in chemically reacting media with an arbitrary number of components.

3.3. Conditions of stability of multicomponent systems with chemical interaction of substances, modified spinodal and critical phase equations

This section examines some aspects of the description of systems with chemical interactions related to alternative approaches to the analysis of thermodynamic stability. First, we will rely on the approach proposed earlier by Zharov in [10] to describe the behavior of systems with one chemical reaction. One of the features of this approach is the use of other concentration variables (not mole fractions). The fundamental equation for the internal energy U, taking into account the condition of chemical equilibrium and one chemical reaction in this case, has the form:

$$dU = TdS - PdV + \sum_{i=1}^{n-1} \mu_i \, dr_i, \qquad (3.3.1)$$

where T – absolute temperature, S – entropy, V – volume, P – pressure, μ_i – chemical potential of a substance i, $r_i = m_i - \nu_i' m_n$, $\nu_i' = \frac{\nu_i}{\nu_n}$, $\mu_i = \left(\frac{\partial U}{\partial r_i}\right)_{S,V,r_{k\neq i}}$, ν_i и ν_n – again stoichiometric coefficients of substances i and n, m_i and m_n – amounts of substances i and n. As in article [10], not molar but mass quantities are considered m_i (in kg). In this case, the chemical potential is determined by the formula $\mu_i = \left(\frac{\partial U}{\partial r_i}\right)_{S,V,r_{k\neq i}}$, and in the equation of a chemical reaction

$$\sum_{i=1}^{n} \nu_i R_i = 0 \qquad (3.3.2)$$

where R_i – substance symbols i and conditions of chemical equilibrium,

$$\sum_{i=1}^{n} \nu_i \mu_i = 0 \qquad (3.3.3)$$

coefficient ν_i is equal to "normal" (when writing in moles of substances) stoichiometric coefficient multiplied by the molecular mass of the substance i. This allows us to simplify further transformations somewhat, taking into account the law of conservation of mass. Note that in the particular case of reactions occurring with conservation of the number of moles, all conclusions will also be valid for ratios in molar quantities. Transition to transformed variables of composition, α_i, can be represented as [10]:

$$\alpha_i = \frac{r_i}{\sum_{i=1}^{n-1} r_i} = x_i - \nu_i' x_n, \qquad (3.3.4)$$

where x_i и x_n – again mass (not mole) fractions of substances. For the sum α_i, in accordance with (3.3.4), the known condition is satisfied [10]:

$$\sum_{i=1}^{n-1} \alpha_i = 1. \qquad (3.3.5)$$

To study the stability of relatively infinitesimal changes in state while maintaining chemical equilibrium (condition (3.3.3)) we will assume the validity of the integral relations for the internal energy, that is, the applicability of Euler's theorem for homogeneous functions of the first degree. Since

$$\sum_{i=1}^{n-1} r_i = m, \qquad (3.3.6)$$

so

$$U = TS - PV + \sum_{i=1}^{n-1} \mu_i r_i. \qquad (3.3.7)$$

Accordingly, the condition of phase stability with respect to continuous changes in state can be written as

$$U' - T''S' + P''V' - \sum_{i=1}^{n-1} \mu_i'' r_i' > 0, \qquad (3.3.8)$$

where indices $'$ and $''$ denote the “initial phase” and the neighboring phase, infinitely close in properties (according to Gibbs – the adjacent state [122, 127]) are designated. After transformations (3.3.8), similar to the analysis of stability in the absence of chemical reactions, we obtain:

$$\Delta T \Delta S - \Delta P \Delta V + \sum_{i=1}^{n-1} \Delta\mu_i \Delta r_i > 0, \qquad (3.3.9)$$

where symbol Δ indicates the difference between the corresponding variables in two states, for example, $\Delta T = T'' - T'$, $\Delta V = V'' - V'$ and so on. It is important that in the general case these are exact infinitesimal differences, i.e., when expanding, for example, in a Taylor series, infinitesimals of higher orders (second, third, fourth, and so on) are taken into account. Relation (3.3.9) is a necessary and sufficient condition for the stability of a chemically equilibrium system with respect to disturbances not associated with a violation of chemical equilibrium. It is obvious that it differs from the classical stability condition by the last sum, which includes not *n*, but *n-1* pair of variables, which is related to the condition of maintaining chemical equilibrium. From (3.3.9) for the second variation of the internal energy $\delta^2 U$, that is, if it is possible to neglect infinitesimals of higher orders, a sufficient condition for stability follows, $\delta^2 U > 0$. This condition, as in the case of systems without reactions, can be represented as a positive definite quadratic form of increments of extensive parameters. Note that here we use the symbol δ, which indicates not a specific change, but any virtual variations of the quantity U that a stable system must satisfy.

From equations (3.3.1) and (3.3.7) it also follows, after the well-known transformations of contact geometry (Legendre transformations) [138], a relation that is a modification of the Gibbs–Duhem equation:

$$SdT - VdP + \sum_{i=1}^{n-1} r_i d\mu_i = 0. \tag{3.3.10}$$

For simplicity and clarity of further conclusions, we will consider a system of three substances under the condition of constant entropy and volume (*S* = const, *V* = const). In this case

$$\delta^2 U = \left(\frac{\partial\mu_1}{\partial r_1}\right)(\delta r_1)^2 + \left(\frac{\partial\mu_1}{\partial r_2}\right)\delta r_1 \delta r_2 + \left(\frac{\partial\mu_2}{\partial r_2}\right)(\delta r_2)^2 + \left(\frac{\partial\mu_2}{\partial r_1}\right)\delta r_2 \delta r_1 > 0 .$$

Accordingly, by Sylvester's theorem, for this quadratic form

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial r_1} & \frac{\partial\mu_1}{\partial r_2} \\ \frac{\partial\mu_2}{\partial r_1} & \frac{\partial\mu_2}{\partial r_2} \end{vmatrix} > 0,\ \frac{\partial\mu_1}{\partial r_1} > 0,\ \frac{\partial\mu_2}{\partial r_2} > 0 \quad . \tag{3.3.11}$$

n the case of a ternary system without reactions of determinants under stability conditions (at *S* = const, *V* = const) can be transformed as follows:

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial m_1} & \frac{\partial\mu_1}{\partial m_2} & \frac{\partial\mu_1}{\partial m_3} \\ \frac{\partial\mu_2}{\partial m_1} & \frac{\partial\mu_2}{\partial m_2} & \frac{\partial\mu_2}{\partial m_3} \\ \frac{\partial\mu_3}{\partial m_1} & \frac{\partial\mu_3}{\partial m_2} & \frac{\partial\mu_3}{\partial m_3} \end{vmatrix} = \left(\frac{\partial\mu_1}{\partial m_1}\right)_{m_2,\, m_3} \left(\frac{\partial\mu_2}{\partial m_2}\right)_{\mu_1, m_3} \left(\frac{\partial\mu_3}{\partial m_3}\right)_{\mu_1, \mu_2} > 0 . \tag{3.3.12}$$

The representation of the form of stability conditions through the product of derivatives (the right-hand side of equality (3.3.12)) is comparatively rarely used in thermodynamic analysis, in comparison with the traditional matrix form. Such a condition was given by Gibbs in his famous work [122], however, without a specific analytical representation (see [122], p. 114]. A number of works [139] are devoted to the analysis of transformations leading to such a representation of the determinant for the general case of a multicomponent system, including those using the apparatus of contact geometry [140-142]. Following [139], the transition from the matrix form in (3.3.11) can be illustrated by the following simple transformations. Let us find the derivative $\left(\frac{\partial\mu_2}{\partial r_2}\right)_{\mu_1}$, based on the system of equations

$$\left.\begin{aligned} d\mu_1 &= \frac{\partial\mu_1}{\partial r_1} dr_1 + \frac{\partial\mu_1}{\partial r_2} dr_2 \\ d\mu_2 &= \frac{\partial\mu_2}{\partial r_1} dr_1 + \frac{\partial\mu_2}{\partial r_2} dr_2 \end{aligned}\right\},$$

$$(dr_2)_{\mu_1} = \frac{\begin{vmatrix} \frac{\partial\mu_1}{\partial r_1} & 0 \\ \frac{\partial\mu_2}{\partial r_1} & (d\mu_2)_{\mu_1} \end{vmatrix}}{\begin{vmatrix} \frac{\partial\mu_1}{\partial r_1} & \frac{\partial\mu_1}{\partial r_2} \\ \frac{\partial\mu_2}{\partial r_1} & \frac{\partial\mu_2}{\partial r_2} \end{vmatrix}} = \frac{\frac{\partial\mu_1}{\partial r_1}(d\mu_2)_{\mu_1}}{D}, \tag{3.3.13}$$

where symbol *D* denotes the denominator in equation (3.3.13). It follows directly from this

$$\left(\frac{d\mu_2}{dr_2}\right)_{\mu_1} = \frac{D}{\left(\frac{\partial\mu_1}{\partial r_1}\right)_{r_2}} .$$

That is

$$\left(\frac{\partial\mu_1}{\partial r_1}\right)_{r_2}\left(\frac{\partial\mu_2}{\partial r_2}\right)_{\mu_1} = \left(\frac{\partial\mu_1}{\partial r_1}\right)_{r_2}\frac{D}{\left(\frac{\partial\mu_1}{\partial r_1}\right)_{r_2}},$$

where

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial r_1} & \frac{\partial\mu_1}{\partial r_2} \\ \frac{\partial\mu_2}{\partial r_1} & \frac{\partial\mu_2}{\partial r_2} \end{vmatrix} = \left(\frac{\partial\mu_1}{\partial r_1}\right)_{r_2}\left(\frac{\partial\mu_2}{\partial r_2}\right)_{\mu_1} > 0. \qquad (3.3.14)$$

This formula can be easily generalized to the case of multicomponent systems with reaction (3.3.2), similar to the work [139]. In brief form, this result can be presented as

$$D = \begin{vmatrix} \frac{\partial\mu_1}{\partial r_1} & \cdots & \frac{\partial\mu_1}{\partial r_{n-1}} \\ \vdots & \ddots & \vdots \\ \frac{\partial\mu_{n-1}}{\partial r_{n-1}} & \cdots & \frac{\partial\mu_{n-1}}{\partial r_{n-1}} \end{vmatrix} = \prod_{i=1}^{n-1}\left(\frac{\partial\mu_i}{\partial r_i}\right)_{\mu_{j=1,\dots,i-1},r_{k=i+1,\dots,n-1}} > 0 \qquad (3.3.15)$$

When moving to concentration variables, equation (3.3.1), taking into account conditions (3.3.5) and (3.3.6), as well as equation (3.3.10), is transformed to the form

$$du = Tds - Pdv + \sum_{i=1}^{n-2}\frac{\partial u}{\partial\alpha_i}d\alpha_i = Tds - Pdv + \sum_{i=1}^{n-2}(\mu_i - \mu_{n-1})d\alpha_i$$

where lowercase letters u, s и v – symbols of parameters related to a unit of mass ("specific" quantities). Accordingly, the quadratic form $\delta^2 u > 0$ includes a smaller number of terms. For clarity, let's consider a system of four substances and again consolidate s and v; derivatives $\frac{\partial u}{\partial\alpha_i}$ let's denote it by the symbol u_i. Then the stability condition takes the form

$$\begin{vmatrix} \frac{\partial u_1}{\partial\alpha_1} & \frac{\partial u_1}{\partial\alpha_2} \\ \frac{\partial u_2}{\partial\alpha_1} & \frac{\partial u_2}{\partial\alpha_2} \end{vmatrix} = \left(\frac{\partial u_1}{\partial\alpha_1}\right)_{\alpha_2}\cdot\left(\frac{\partial u_2}{\partial\alpha_2}\right)_{u_1} > 0.$$

Since, while maintaining the number of moles during the reaction, for example, $R_1 + R_2 = R_3 + R_4$, with the stoichiometry of esterification processes [9, 143], the ratios written in mass units (in kg) will also be valid in molar units. Accordingly, the transformed concentration variables, α_i, can be referred to as molar quantities (mole fractions x_i):

$$\left.\begin{array}{l} \alpha_1 = x_1 + x_4 \\ \alpha_2 = x_2 + x_4 \\ \alpha_3 = x_3 - x_4 \end{array}\right\},$$

At the stability boundary (3.3.14), as well as (3.3.15), vanishes. The equality to zero of the stability determinant in the case of systems without reactions is discussed in detail in the literature [124, 126, 127, 144]. It is known that upon reaching the stability boundary, it is the determinant that vanishes, and not its diagonal elements, minors $\frac{\partial\mu_1}{\partial m_1}$ и $\frac{\partial\mu_2}{\partial m_2}$ in (3.3.14). This mathematical conclusion can naturally be extended to the case under consideration of a system with a chemical reaction (while maintaining chemical equilibrium). In connection with the form (3.3.14) and (3.3.15), the question arises about the conditions of the stability boundary determined by the right-hand side of the equality. We will show that when the first derivative reaches the indicated boundary, the second one vanishes, $\left(\frac{\partial\mu_2}{\partial r_2}\right)_{\mu_1}$ in (3.3.14).

Indeed, the first of the derivatives, $\left(\frac{\partial\mu_1}{\partial r_1}\right)_{r_2}$, is the diagonal minor of the determinant in (3.3.14). Accordingly, the equation of the stability boundary (spinodal) is the equality

$$\left(\frac{\partial\mu_2}{\partial r_2}\right)_{\mu_1} = 0. \tag{3.3.16}$$

The above result is generalized to the case of an arbitrary number of substances and independent parameters, as a consequence of (3.3.15). It should be borne in mind that the derivatives of intensive quantities must be considered, since the conclusions are based on the fundamental equation for internal energy. In addition, as indicated in [127], extensive parameters can change even when intensive quantities are constant (for example, a change in the total mass). In the general case, the stability boundary can be represented through the derivatives of any intensive quantity with respect to the extensive one. For example, one of the conditions

$$\left(\frac{\partial\mu_1}{\partial r_1}\right)_{T,V,\mu_2,\,\mu_3,\dots\,\mu_{n-1}} = 0 \tag{3.3.17}$$

at the same time means that at the stability boundary a known condition is fulfilled (for systems without reactions [127]):

$$dT = dP = d\mu_1 = d\mu_2 = \cdots = 0,$$

that is, in this case (while maintaining chemical equilibrium) at the stability boundary, with neglect of infinitesimals of higher orders, an indifferent (neutral) equilibrium is established [127]. Note that in equality (3.3.16) and other similar conditions (3.3.17) all independent intensive parameters are fixed, except one, in this case, V, and not P. This is due to the known thermodynamic limitations arising from the Gibbs-Duhem equation (3.3.10).

The obtained results should be attributed to alternative formulations of the conditions of thermodynamic stability of systems with chemical interaction of components (while maintaining chemical equilibrium). In other words, the stability of chemically equilibrium systems with respect to non-chemical disturbances is considered [98]. A feature of the considered forms of stability conditions is their analysis not only on the basis of the stability matrix, but also as a result of the transformation of the stability determinant into the product of partial derivatives of intensive parameters [145]. This modification of the stability conditions makes it possible to present in a new form the stability boundaries, in fact, the spinodal equation in chemically equilibrium systems and the first equation of the critical phase. The results may have a certain significance for the development of stability theory, including studies of critical states of multicomponent systems.

3.4. About the stability boundary

As is known, the critical state belongs simultaneously to the binodal and spinodal, respectively, the first equation of the critical phase can be represented as the equation of the stability boundary with respect to continuous changes in state. Therefore, the analysis of the stability boundary is simultaneously a study of the properties of the critical state. Although the conditions of thermodynamic stability have been well studied, equally, in physicochemical and mathematical respects, some provisions of the theory, as will be shown below, require clarification. In particular, one of the problems, from our point of view, raising some questions, is the analysis of the boundaries of thermodynamic stability. These conclusions were made within the framework of our work, during the analysis of the equations of the critical phase [146]. Let us consider these aspects in more detail. The inclusion of the concept of stability in the apparatus of general thermodynamics is largely associated with the works of Gibbs, whose merit is the very definition of thermodynamic equilibrium and its stability [122]. The initial provisions of thermodynamic theory formally coincide with the concepts of equilibrium and stability in analytical mechanics, more precisely, with the extremal principles of mechanics. The main difference of thermodynamic stability analysis is associated with the use of the consequences of the second law of thermodynamics both for the formulation of the stability criteria themselves and for particular conclusions and important physical and chemical results.

An obvious condition for the stability boundary is the equality to zero of the expression, which is, according to Gibbs, the stability criterion [122]. Further, we will consider the condition of stability with respect to continuous changes in state, that is, infinitesimal changes. Such a restriction, as indicated, for example, in [126], allows us to obtain more general conclusions, since it includes the study of the stability of both stable and metastable states. Otherwise, the analysis of metastable states, by their definition, requires the use of data on the limits within which these states exist. In addition, it is sufficient to consider the stability of homogeneous states: their analysis is easily extended to heterogeneous states, with some additional nuances [127]. In a fairly general form, this stability condition, following Gibbs [122], can be represented as

$$U'' - \sum_i X_i' Y_i'' > 0, \qquad (3.4.1)$$

where U – internal energy, X_i – intensive parameter, Y_i – conjugate extensive parameter, quantities with one prime refer to the state being studied for stability, and quantities with two primes refer to the neighboring virtual state. We emphasize that, unlike a number of studies, for example, [122, 126, 127], in which it is assumed that the neighboring state is a real infinitely close state, we do not introduce such restrictions on the virtual state. Apparently, this is more consistent with Gibbs's original idea of the stability criterion [122]. We also note that in formula (3.4.1), as in other studies of stability, including [122], the validity of the integral forms of the fundamental equations is assumed, which is a certain known limitation (the applicability of Euler's theorem on homogeneous functions). The case of equilibrium between the original and virtual phases, i.e. the corresponding phase equilibrium, is also excluded. For simplicity and clarity, we will further restrict ourselves to the "standard set" of thermodynamic parameters and present (3.4.1) in equivalent forms [122]:

$$U'' - U' > T'(S'' - S') - P'(V'' - V') + \mu_1'(m_1'' - m_1') + \cdots + \mu_n'(m_n'' - m_n') \qquad (3.4.2)$$

or

$$-T'S'' + P'V'' - \mu_1' m_1'' - \cdots - \mu_n' m_n'' + T''S'' - P''V'' + \mu_1'' m_1'' + \cdots + \mu_n'' m_n'' > 0, \qquad (3.4.3)$$

Note that the pressure in formula (3.4.1) should be represented as (-*P*), that is, with a minus sign.

Equation (3.4.3) is transformed to the known form [127]:

$$(T'' - T')S'' - (P'' - P')V'' + (\mu_1'' - \mu_1')m_1'' + \cdots + (\mu_n'' - \mu_n')m_n'' > 0, \qquad (3.4.4)$$

which actually coincides with one of the Gibbs stability conditions [147]. Since the differences in brackets in (3.4.4) are infinitesimal exact differences, then, neglecting the infinitesimals of higher orders, we move on to differentials and write:

$$S''dT - V''dP + m_1''d\mu_1 + \cdots + m_n''d\mu_n \geq 0. \qquad (3.4.5)$$

Sign ≥ in formula (3.4.5) appeared because, unlike (3.4.4), formula (3.4.5) does not take into account the contribution of infinitesimal higher orders. As a result, (3.4.5) is only a necessary condition for the stability of phase (′) with respect to continuous changes in state. It is obvious that the left-hand side of (3.4.5) coincides in form with the left-hand side of the Gibbs-Duhem equation [124, 126]:

$$SdT - VdP + m_1 d\mu_1 + \cdots + m_n d\mu_n = 0. \qquad (3.4.6)$$

Nevertheless, the difference between (3.4.5) and (3.4.6) is quite obvious. Formula (3.4.5), like formula (3.4.4), characterizes a virtual disturbance of the state, which in the general case is not an equilibrium one. Formula (3.4.6) refers to an equilibrium change in the state. Accordingly, stability analysis cannot be carried out on the basis of condition (3.4.6). In the literature, this important point is ignored, which leads to significant inaccuracies, or to the reduction of stability conditions to a special case. For example, in the book [124, chapter 15, paragraph 14] a derivation and conclusion are given about the zeroing of the stability determinant (at T, P = const) - partial derivatives in the Jacobian are calculated from the Gibbs - Duhem equation. Obviously, in this case a special case of equilibrium displacement is considered. First, we also note that equation (3.4.6) is quite compatible with one of the conditions of the stability boundary considered by Gibbs, namely, the relation that determines neutral equilibrium [122, 127]:

$$dT = dP = d\mu_1 = \cdots d\mu_n = 0. \qquad (3.4.7)$$

Another important aspect of the stability analysis of a thermodynamic system is related to the introduction or selection of a parameter that allows one to exclude changes associated with an increase/decrease only in the mass of the system, and not its state, i.e. intensive parameters. Such a “scale factor” [144] can be, for example, the volume or total mass of the system [122]. Such a selection of one of the parameters (in the case of volume) in the stability analysis based on formulas (3.4.3 – 3.4.5) is obviously unnecessary, since all extensive parameters are already fixed in these relations. Nevertheless, in all publications known to us, for example [122, 126, 127], when considering stability, the indicated “scale factor” is introduced in one form or another, possibly in order to circumvent the condition of “zeroing” the determinant. It is also not entirely clear what Gibbs had in mind when discussing the stability condition

$$\Delta U > T\Delta S - P\Delta V + \mu_1 \Delta m_1 + \cdots + \mu_n \Delta m_n \qquad (3.4.8)$$

(formula (145) in [122], p. 106) and asserting that “if only the amount of substance in the body changes, which determines the value of the variables, and not the phase of the body, then the value of the left-hand side of (145) will obviously be zero” ([123], p. 110). In the original ([122], p. 106): «If only the quantity of the body which determines the value of the variables should vary and not its phase, the value of the first member of (145) would evidently be zero». It is obvious that the value of the left-hand side of (3.4.8), i.e. the change in the internal energy of the system, when its mass changes will not be zero, but will also change. Here, as before, the formulas from Gibbs's works are given in accordance with modern notations.

As we have already noted above, the determinant that determines stability, in accordance with the condition $\delta^2 U > 0$, that is, the Hessian (for the set of n+2 pairs of parameters we selected above)

$$\begin{vmatrix} \frac{\partial^2 U}{\partial Y_1^2} & \frac{\partial^2 U}{\partial Y_1 \partial Y_2} & \cdots & \frac{\partial^2 U}{\partial Y_1 \partial Y_{n+2}} \\ \frac{\partial^2 U}{\partial Y_2 \partial Y_1} & \frac{\partial^2 U}{\partial Y_2^2} & \cdots & \frac{\partial^2 U}{\partial Y_2 \partial Y_{n+2}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial Y_{n+2} \partial Y_1} & \frac{\partial^2 U}{\partial Y_{n+2} \partial Y_2} & \cdots & \frac{\partial^2 U}{\partial Y_{n+2}^2} \end{vmatrix} > 0 \tag{3.4.9}$$

in the general case it is not equal to zero, since the derivatives included in it are taken during the disturbance of equilibrium and, accordingly, are not related by the relations

$$\left.\begin{array}{c} Y_1 \frac{\partial^2 U}{\partial Y_1^2} + Y_2 \frac{\partial^2 U}{\partial Y_1 \partial Y_2} + \cdots + Y_{n+2} \frac{\partial^2 U}{\partial Y_1 \partial Y_{n+2}} = 0 \\ Y_1 \frac{\partial^2 U}{\partial Y_2 \partial Y_1} + Y_2 \frac{\partial^2 U}{\partial Y_2^2} + \cdots + Y_{n+2} \frac{\partial^2 U}{\partial Y_2 \partial Y_{n+2}} = 0 \\ \vdots \\ Y_1 \frac{\partial^2 U}{\partial Y_{n+2} \partial Y_1} + Y_2 \frac{\partial^2 U}{\partial Y_{n+2} \partial Y_2} + \cdots + Y_{n+2} \frac{\partial^2 U}{\partial Y_{n+2}^2} = 0 \end{array}\right\}, \tag{3.4.10}$$

which are consequences of the Gibbs-Duhem equation

$$Y_1 d \frac{\partial U}{\partial Y_1} + Y_2 d \frac{\partial U}{\partial Y_2} + \cdots + Y_{n+2} d \frac{\partial U}{\partial Y_{n+2}} = 0. \tag{3.4.11}$$

It is the particular variants of relations (3.4.10) that were used in [124] to prove, also for particular cases (T, P = const), the identical equality to zero of the determinant of the quadratic form of increments of extensive parameters.

Accordingly, since it is the determinant (3.4.9) that first vanishes, and not its minors, the stability boundary is its equality to zero. It is important that in the above derivations the condition of constancy of one of the parameters or their combination, for example, the total amount of substances, was not used. The correctness of the result is also obvious from the fact that (3.4.9) includes derivatives of intensive quantities (with respect to extensive parameters).

Finally, let us consider another condition of the stability boundary, obtained by transforming the determinant (3.4.9) into a product of partial derivatives

$$\begin{vmatrix} \frac{\partial^2 U}{\partial Y_1^2} & \frac{\partial^2 U}{\partial Y_1 \partial Y_2} & \cdots & \frac{\partial^2 U}{\partial Y_1 \partial Y_{n+2}} \\ \frac{\partial^2 U}{\partial Y_2 \partial Y_1} & \frac{\partial^2 U}{\partial Y_2^2} & \cdots & \frac{\partial^2 U}{\partial Y_2 \partial Y_{n+2}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial Y_{n+2} \partial Y_1} & \frac{\partial^2 U}{\partial Y_{n+2} \partial Y_2} & \cdots & \frac{\partial^2 U}{\partial Y_{n+2}^2} \end{vmatrix} = \prod_{i=1}^{n+2} \left(\frac{\partial^2 U}{\partial Y_i^2} \right)_{\frac{\partial U}{\partial Y_{j=1,\ldots i-1}},\ Y_{k=i+1,\ldots,n+2}} > 0 \tag{3.4.12}$$

Despite the fact that the determinant, as follows from (3.4.12), vanishes when any of the factors is equal to zero, the stability boundary condition must correspond to the specified equality of one specific factor.

For greater clarity, let us consider a binary system, presenting, in addition, Y_1 and derivatives $\frac{\partial^2 U}{\partial Y_i^2}$ through specific variables:

$$\begin{vmatrix} \frac{\partial T}{\partial S} & \frac{\partial T}{\partial V} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial(-P)}{\partial S} & \frac{\partial(-P)}{\partial V} & \frac{\partial(-P)}{\partial m_1} & \frac{\partial(-P)}{\partial m_2} \\ \frac{\partial \mu_1}{\partial S} & \frac{\partial \mu_1}{\partial V} & \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_1}{\partial m_2} \\ \frac{\partial \mu_2}{\partial S} & \frac{\partial \mu_2}{\partial V} & \frac{\partial \mu_2}{\partial m_1} & \frac{\partial \mu_2}{\partial m_2} \end{vmatrix} =$$

$$= \left(\frac{\partial T}{\partial S}\right)_{V,m_1,m_2} \cdot \left(\frac{\partial(-P)}{\partial V}\right)_{T,m_1,m_2} \cdot \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,P,m_2} \cdot \left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,p,\mu_1} > 0 \qquad (3.4.13)$$

Multiplier $\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,p,\mu_1}$ in this relation, at first glance, is equal to zero, in accordance with the Gibbs-Duhem equation (3.4.6). However, this is not the case, since, as before, we are considering a nonequilibrium virtual disturbance for which equation (3.4.5) is satisfied. Let us show that the equality to zero of precisely this derivative corresponds to the stability boundary. First of all, we note that the determinant in (3.4.13) can be represented as a product of derivatives in various ways. The sequence of pairs of parameters is not limited to that given in relation (3.4.13). For example, it is obvious that

$$\left(\frac{\partial T}{\partial S}\right)_{V,m_1,m_2} \cdot \left(\frac{\partial(-P)}{\partial V}\right)_{T,m_1,m_2} \cdot \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,P,m_2} \cdot \left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,p,\mu_1} = \left(\frac{\partial \mu_2}{\partial m_2}\right)_{S,V,m_1} \cdot \left(\frac{\partial \mu_1}{\partial m_1}\right)_{S,V,\mu_2} \cdot \left(\frac{\partial(-P)}{\partial V}\right)_{S,\mu_1,\mu_2} \cdot \left(\frac{\partial T}{\partial S}\right)_{P,\mu_1,\mu_2}. \qquad (3.4.14)$$

Other combinations of derivatives under the transformation of the determinant (3.4.13) are also possible. In this case, provided that $\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,p,\mu_1} = 0$ other similar conditions will also apply, namely:

$$\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,p,\mu_1} = \left(\frac{\partial T}{\partial S}\right)_{P,\mu_1,\mu_2} = \left(\frac{\partial(-P)}{\partial V}\right)_{T,\mu_1,\mu_2} = \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,P,\mu_2} = 0. \qquad (3.4.15)$$

As was pointed out in the work of Gibbs [122] and subsequent studies [127], the relations (3.4.15) or their consequences are, neglecting infinitesimals of higher orders, conditions of neutral equilibrium. In this case (neutral equilibrium) we can already use the results for equilibrium changes, for example [37, 101, 141, 143, 148-153]:

$$\left(\frac{\partial X_i}{\partial Y_i}\right)_{Y_1,Y_2,\dots,Y_{i-1},Y_{i+1},\dots,Y_{n+1},Y_{n+2}} \geq \left(\frac{\partial X_i}{\partial Y_i}\right)_{Y_1,Y_2,\dots,Y_{i-1},Y_{i+1},\dots,Y_{n+1},X_{n+2}} \geq \cdots \geq$$
$$\geq \left(\frac{\partial X_i}{\partial Y_i}\right)_{Y_1,X_2,\dots,X_{i-1},X_{i+1},\dots,X_{n+2}} \left(\frac{\partial X_i}{\partial Y_i}\right)_{X_1,X_2,\dots,X_{i-1},X_{i+1},\dots,X_{n+2}} = 0. \qquad (3.4.16)$$

Note that in this case, taking into account the previous discussion, we have expanded the options for fixing independent parameters (in comparison with [37, 101, 141, 143, 148-153]), including in (3.4.16) the condition $X_1, X_2, \dots, X_{i-1}, X_{i+1}, \dots, X_{n+2} = const$. From inequalities (3.4.16) it follows that, in particular, for the derivatives in relation (3.4.13) at the stability boundary the following conditions are satisfied:

$$\left(\frac{\partial T}{\partial S}\right)_{V,m_1,m_2} \geq \left(\frac{\partial T}{\partial S}\right)_{P,\mu_1,\mu_2} = 0,$$

$$\left(\frac{\partial(-P)}{\partial V}\right)_{T,m_1,m_2} \geq \left(\frac{\partial(-P)}{\partial V}\right)_{T,\mu_1,\mu_2} = 0, \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,P,m_2} \geq$$

$$\geq \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,P,\mu_2} = 0. \qquad (3.4.17)$$

Thus, we have proved that all factors in the relation (3.4.16) will be greater than the last of them, $\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,p,\mu_1}$, which defines the stability boundary. Obviously, this result can be easily generalized to the case of an arbitrary number of thermodynamic parameters. In all cases, the condition for the stability boundary is the equality to zero of the determinant in formula (3.4.13), or the condition

$$\left(\frac{\partial^2 U}{\partial Y_i^2}\right)_{\frac{\partial U}{\partial Y_1}, \frac{\partial U}{\partial Y_2}, \ldots, \frac{\partial U}{\partial Y_{i-1}}, \frac{\partial U}{\partial Y_{i+1}}, \ldots, \frac{\partial U}{\partial Y_{n+2}}} = \left(\frac{\partial^2 U}{\partial Y_i^2}\right)_{X_1, X_2, \ldots, X_{i-1}, X_{i+1}, \ldots, X_{n+2}} = 0.$$

These conditions, in general, coincide with the results of Gibbs [122] and the conclusions of subsequent works, for example, [127], defining the stability boundary as a state of neutral equilibrium (with neglect of infinitesimals of higher orders). Note that special cases, when higher order variations should be taken into account, for example, in a critical state, require additional analysis. From our point of view, the presented analysis of the stability boundaries, to which the critical state also corresponds, gives a clearer and more correct idea of the stability conditions themselves. Indeed, it is unjustified to involve in the analysis of a nonequilibrium virtual perturbation the relations established for an equilibrium displacement, such as the Gibbs-Duhem equation. The presented version of the derivation of the conditions of the stability boundaries assumes a departure from equilibrium during a virtual perturbation of the state of the system. At the same time, the final conclusions, in general, coincide with the classical results, according to which a neutral (indifferent) equilibrium is realized at the stability boundary, with the possibility of neglecting variations in the internal energy of higher orders.

3.5. Simultaneous phase and chemical equilibrium

As indicated above, the chemical equilibrium of the reaction between three substances in a homogeneous system under isothermal-isobaric conditions corresponds to a curve in the composition triangle. At variables T and P, the chemical equilibrium corresponds to a hypersurface in a four-dimensional space (composition – T – P). At a constant temperature (or constant pressure), the chemical equilibrium is represented as a surface in the corresponding three-dimensional space.

In the case of a reaction between four substances, the chemical equilibrium in a homogeneous system under isothermal-isobaric conditions is represented as a surface in a concentration tetrahedron. Even at a variable temperature (or variable pressure), the graphical representation of such a chemical equilibrium is difficult, since it will correspond to a hypersurface in thermodynamic space.

For states of simultaneous chemical and phase equilibrium in a two-phase system with the possibility of its shift with a change in temperature and pressure, it follows from the phase rule, $f = n + 2 - r - k = n + 2 - 2 - 1 = n - 1$, that a three-component system has two degrees of freedom (bivariant equilibrium), and a quaternary system has three degrees of freedom. Under isothermal-isobaric conditions (T, P = *const*) and simultaneous chemical and phase equilibrium, the quaternary two-phase system is in a monovariant equilibrium, which corresponds to the curve in the composition tetrahedron on the state diagram.

The objects of our experimental studies were systems of four substances with reactions of synthesis-hydrolysis of carboxylic acid esters

$$Alcohol(R_1) + Acid(R_2) = Water(R_3) + Ester(R_4).$$

It should be noted that the analysis of specific experimental data and its results presented below can be extended to other systems with similar chemical reaction stoichiometry. According to the equation of these reactions, all four ternary subsystems:

$R_1 - R_2 - R_3$, $R_1 - R_2 - R_4$, $R_1 - R_3 - R_4$, $R_2 - R_3 - R_4$

are only in a chemically nonequilibrium state, therefore the compositions of all three-component reaction mixtures cannot belong to the surface of chemical equilibrium. It is obvious that two of the six binary subsystems, "acid - alcohol" and "water - ether" ($R_1 - R_2$ и $R_3 - R_4$), are also chemically nonequilibrium. In the other four binary subsystems ($R_1 - R_3$, $R_1 - R_4$, $R_2 - R_3$, $R_2 - R_4$) there is no chemical reaction, therefore the edges of the tetrahedron of compositions corresponding to these binary systems, as well as all four vertices of the tetrahedron are the boundaries of the surface of chemical equilibrium. At the same time, in accordance with the above, the faces and edges of the concentration tetrahedron corresponding to all ternary and two binary subsystems cannot belong to this surface ($R_1 - R_2$ и $R_3 - R_4$). Thus, the surface of chemical equilibrium of the reaction $R_1 + R_2 = R_3 + R_4$ in a homogeneous system it is located as a whole inside the tetrahedron of compositions and rests only on four edges corresponding to binary systems without chemical reactions.

Curves, surfaces and hypersurfaces of chemical equilibrium are a special case of isoaffine (from *affinity* – affinity) manifolds that correspond not to zero (equilibrium), but to some constant value of affinity in a chemically nonequilibrium state:

$$A = -\sum_{i=1}^{n} \nu_i \mu_i = const. \tag{3.5.1}$$

Such manifolds are also elements of the state diagrams of systems with chemical reactions, in contrast to systems without reactions. The specified manifolds also represent curves, surfaces or hypersurfaces in the corresponding concentration space. The complexity of the graphical representation of thermodynamic properties for the states of chemical equilibrium of multicomponent systems (and the impossibility in the case of hypersurfaces) determined the introduction of transformed concentration variables (also called "α-variables") to describe chemically equilibrium compositions. The thermodynamic derivation, first presented in the work [10], was based on the natural reduction of independent variables in a chemically equilibrium system: while maintaining chemical equilibrium: the number of thermodynamic degrees of freedom is reduced by k (equilibrium with respect to k chemical reactions). Accordingly, the number of concentration variables can be, in the case of one reversible chemical reaction, reduced by one. The rationale for introducing new composition variables in the original article [10] was presented on the basis of an analysis of fundamental thermodynamic equations. The application options of α-variables for thermodynamic analysis of reaction systems of various types were subsequently considered in many works, primarily in the studies of the Moscow State University of Fine Chemical Technologies named after M.V. Lomonosov and the St. Petersburg State University, for example, [9, 98, 143, 154, 155] and others. As already indicated, practically the same transformed concentration variables were much later proposed by Barbosa and Docherty based on material balance equations [156]. In the particular case under consideration of a system of four substances with esterification/hydrolysis reactions

$$\sum_{i=1}^{n} \nu_i R_i = \sum_{i=1}^{4} \nu_i R_i = -R_1 - R_2 + R_3 + R_4 = 0 \qquad (3.5.2)$$

($\nu_1 = -1,\ \ \nu_2 = -1,\ \ \nu_3 = +1,\ \ \nu_4 = +1$) transformed variables of composition (*α*-variables) have the form:

$$\alpha_1 = x_1 + x_4$$
$$\alpha_2 = x_2 + x_4\ .$$
$$\alpha_3 = x_3 - x_4$$

It is obvious that the following conditions are also met:

$$\alpha_1 + \alpha_2 + \alpha_3 = 1,$$
$$0 < \alpha_1 < +1$$
$$0 < \alpha_2 < +1 \quad .$$
$$-1 < \alpha_3 < +1$$

Thus, instead of a three-dimensional concentration simplex (composition tetrahedron), the concentration space will be a square of α-variables – a two-dimensional complex of compositions.

Analysis of the intersection of the manifolds of phase and chemical equilibrium in the concentration space is of practical interest when considering stratified solutions. Such an intersection of thermodynamic surfaces reflects the fact of establishing chemical equilibrium in both the homogeneous and heterogeneous regions of the reaction mixture compositions. A simple illustration can be presented for a three-component system: in this case, the intersection of the binodal and the chemical equilibrium curve is considered.

Fig. 3.5.1 shows one of the possible variants of the diagram of such a system as a visual example. In this case, during the reaction

$$\sum_{i=1}^{3} \nu_i R_i = \nu_1 R_1 + \nu_2 R_2 + \nu_3 R_3 = 0\,,$$

where coefficient ν_3 has a sign opposite to the signs of the coefficients ν_1 и ν_2, or, in another form,

$$|\nu_1| R_1 + |\nu_2| R_2 = |\nu_3| R_3$$

for some compositions of the reacting mixture, chemical equilibrium is achieved in the stratification region - in the two-phase heterogeneous region.

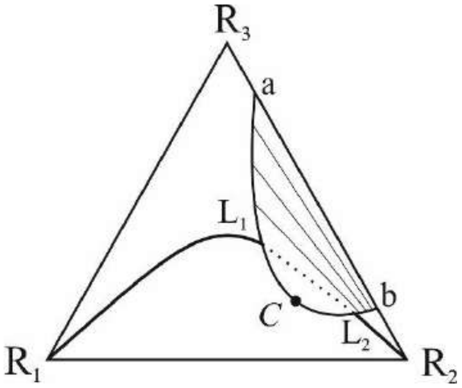

Fig. 3.5.1. Schematic diagram of a three-component system with a chemical reaction $|\nu_1|R_1+|\nu_2|R_2=|\nu_3|R_3$, chemical equilibrium in which is established both in homogeneous and heterogeneous regions of composition. a-b – binodal, R_1-R_2 – chemical equilibrium curve, straight lines are liquid-liquid tie-lines, *C* – critical point of liquid-liquid equilibrium, dotted line L_1–L_2 – special (unique) reaction tie-line.

The true compositions of the phases of a chemically equilibrium heterogeneous mixture in Fig. 3.5.1 correspond to the points L_1 and L_2 on binodal; The gross compositions of chemically equilibrium compositions will belong to the tie-line L_1–L_2. Such tie-lines were called unique (or special) reactive liquid–liquid tie-line in the article [103]. Later, in the work [134], using model calculations, a specific example of a ternary system was given in which chemical equilibrium is established in both the homogeneous and heterogeneous regions (cyclohexane + water = cyclohexyl alcohol).

As for quaternary systems, the work [157] presents a diagram of open evaporation, including homogeneous and heterogeneous regions of chemical equilibrium of the reaction of n-propyl laurate synthesis. Note that, strictly speaking, the shift in the composition of the solution on the surface of chemical equilibrium should be considered not only as open evaporation, but as a result of the combined reaction-mass exchange process "reaction + evaporation". Our experimental results are considered in the following sections. Here we also note our publications concerning the analysis of some structures of diagrams of ternary systems, works [37, 38], which present an analysis of the diagrams given earlier in the article [135]. The figure from the article [37] (analogous to the figure from the article [135]) is given below.

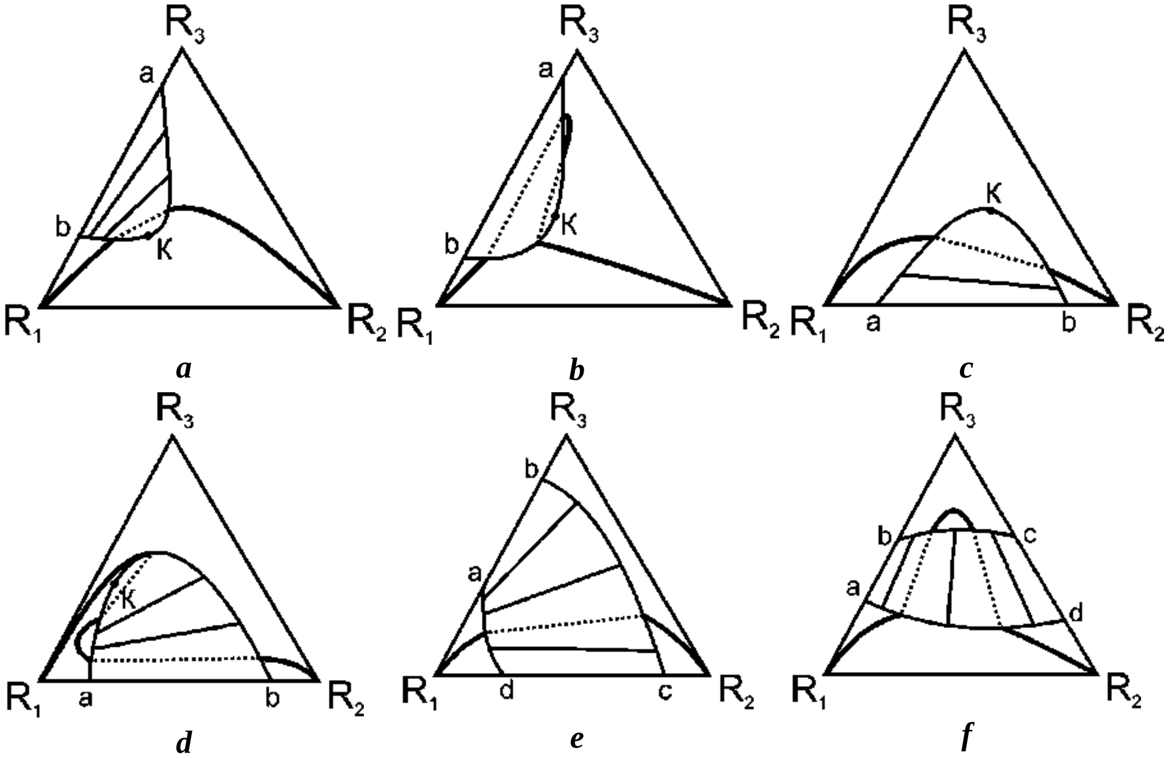

Fig. 3.5.2. Variants of mutual arrangement of chemical equilibrium curves (▬) and binodals (—) in the concentration triangle. ▪▪▪▪ – tie-line connecting the intersection points of the chemical equilibrium curve and the binodal ("unique reactive tie-line"), K – critical point, ab and cd are the solubility limits in a binary system.

Of particular interest is also the analysis of the change in affinity in reaction systems taking into account the arrangement of tie-lines and binodals. Some of our results in this area are published in [38].

We note again that the current base of directly experimental data on combined liquid-liquid equilibria and chemical equilibrium is quite limited. Although a wide range of chemically reacting heterogeneous systems is significant for technological practice, the complexity of experimental studies determines the limitations and incompleteness of the experimental data obtained. Some works are related to the development of options for organizing technological processes of reactive rectification and extraction, but do not contain sufficiently detailed experimental information on phase equilibria and thermodynamic properties. Of course, due to the understandable experimental difficulties of a complete and detailed study of phase and chemical equilibrium in systems including five or more substances (the need for a very large volume of data), as well as in systems with several chemical reactions, it is advisable to use computational methods of thermodynamic modeling to solve technological problems. The parameters of the models can be determined or refined on the basis of experimental data on simpler subsystems. Typically, these studies are aimed at solving problems of organizing the processes of reactive rectification, extraction and other combined processes, see, for example, articles [158-160].

One of the problems associated with the experimental study of phase equilibria during chemical reactions is the shift in the composition of the solution under study due to the chemical reaction. In this regard, the difference in the views of the authors of publications on the possibilities of directly determining the parameters of phase equilibrium in chemically reacting media is noteworthy. In our study and, as a rule, in other publications, when studying chemically nonequilibrium mixtures formed by reagents and products of the esterification reaction, it is assumed that in the absence of a catalyst the reaction can be neglected: the shift in the composition due to its occurrence during the experiment is insignificant. This is not always true when studying binary acid-alcohol systems. For example, in the case of relatively fast reactions in the presence of formic acid, certain amounts of reaction products are detected, but we do not consider these systems further. In other systems, the reaction progress was monitored. Some simplifications are associated with the fact that in the case of combined phase and chemical equilibrium in a quaternary system, the liquid-liquid equilibrium is studied in the immediate vicinity of chemical equilibrium, where reactions are always significantly slowed down. In Fig. 3.5.3 shows a typical general view of the surface of chemical equilibrium and the binodal surface, their arrangement in the tetrahedron of compositions for systems with the reaction of esterification-hydrolysis of the ester. Fig. 3.5.4 schematically shows the diagrams in the concentration tetrahedron and square α- variables, with the area of intersection of the chemical equilibrium surface and the binodal (the shaded area inside the closed curve **C_1 - C_2** on Fig. 3.5.4a). For clarity, this area is shown separately in Fig. 3.5.4b.

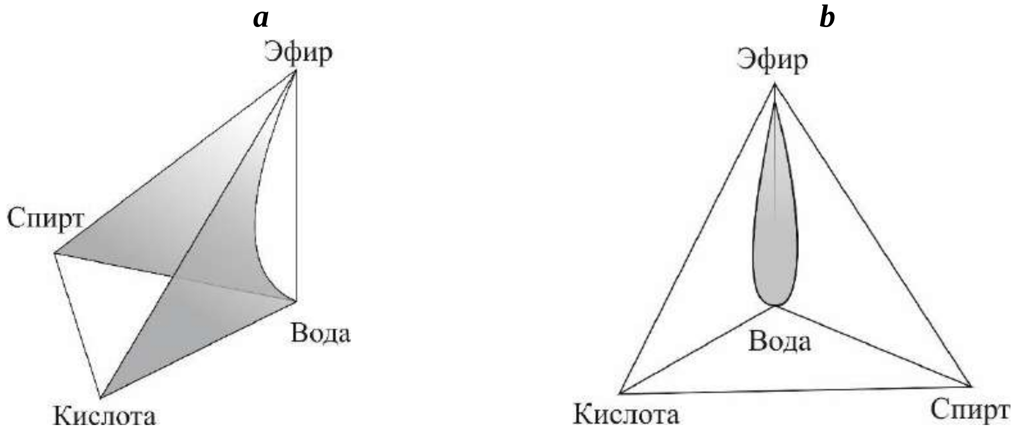

Fig. 3.5.3. General view of chemical equilibrium surfaces (*a*) and binodal surface (*b*) in a system with an esterification reaction

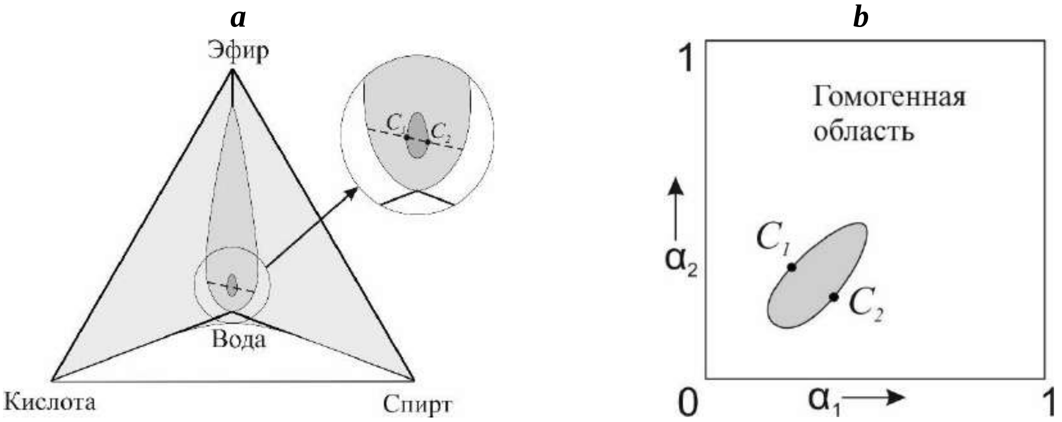

Fig. 3.5.4. The intersection region of the chemical equilibrium surface and the binodal surface in a system with an esterification reaction (explanations in the text) in a concentration tetrahedron (*a*) and in the square of α-variables (*b*). C_1, C_2 – critical points of liquid-liquid equilibrium, also corresponding to chemically equilibrium compositions; --- critical curve in a concentration tetrahedron.

The region of stratification of a chemically equilibrium liquid mixture also determines the existence of chemically equilibrium critical liquid-liquid states, which are considered further using our specific experimental data as an example. In conclusion of this section, we note that in modern works, sufficient attention is paid to the kinetics of nonequilibrium chemical reactions. At the same time, even in articles devoted to the substantiation and organization of reactive rectification processes, when the patterns of kinetic behavior are important for assessing not only equilibrium but also stationary parameters, the main attention is paid to homogeneous systems. The problems of the kinetics of chemical processes in a heterogeneous liquid-phase system with the maintenance (restoration) of phase equilibrium deserve separate consideration, which goes beyond the scope of the thesis. Other issues related to the general problems of studying combined phase and chemical equilibrium were considered in our review articles [11, 12].

3.6. Critical states of liquid-liquid equilibria - experimental data (discussion)

3.6.1. Critical phases in ternary systems

The main focus of the thesis is on the study of combined phase and chemical equilibria. These are, in the absolute majority, systems of four substances. Therefore, in this subparagraph we will limit ourselves to stating the data we obtained for ternary systems. We will also note that we do not have examples of combined phase (liquid-liquid) and chemical equilibrium in ternary systems. The diagrams given in the articles [134, 161] were obtained as a result of calculations, and not direct experimental studies. The set of data we obtained on critical liquid-liquid states (not in chemical equilibrium) in ternary systems is large, therefore only examples of such results are given below, with brief comments. In total, we obtained data on 34 three-component critical points. The n-propyl alcohol – n-propyl acetate – water system has been studied in sufficient detail, including earlier, in the works of N.A. Smirnova and co-authors [162-163], under isothermal and isobaric conditions. Our data [41, 42, 45, 46, 107, 109] relate to other temperatures, with special attention, as indicated earlier, given to the precise determination of critical points. One example is shown in Fig. 3.6.1.1. This is a typical diagram for ternary systems, with stratification in one of the binary subsystems (n-propyl acetate – water). The region of liquid–liquid equilibrium is adjacent to the ether–water side and is limited by the solubility curve [45, 107, 109] with the critical point [45, 107]. Similar diagrams for this system, at other temperatures, are given in the original articles based on the thesis materials (see the list of publications).

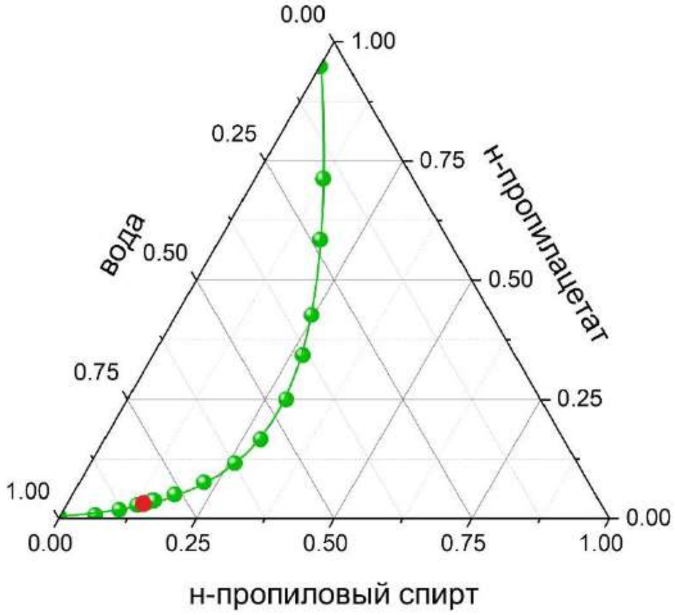

Fig. 3.6.1.1. Solubility (●) [107] and the critical point (●) [45, 107] in the system n-propyl alcohol – n-propyl acetate – water at 293.15 K, mole fractions.

For the acetic acid – n-propyl acetate – water system, the compositions of the coexisting phases at a temperature of 313.15 K were previously found [164]. Our data, articles [41, 42, 45, 109], presented in Fig. 3.6.1.2, show that, in general, the structure of the equilibrium diagrams in this system is not fundamentally different from the n-propyl alcohol – n-propyl acetate – water system.

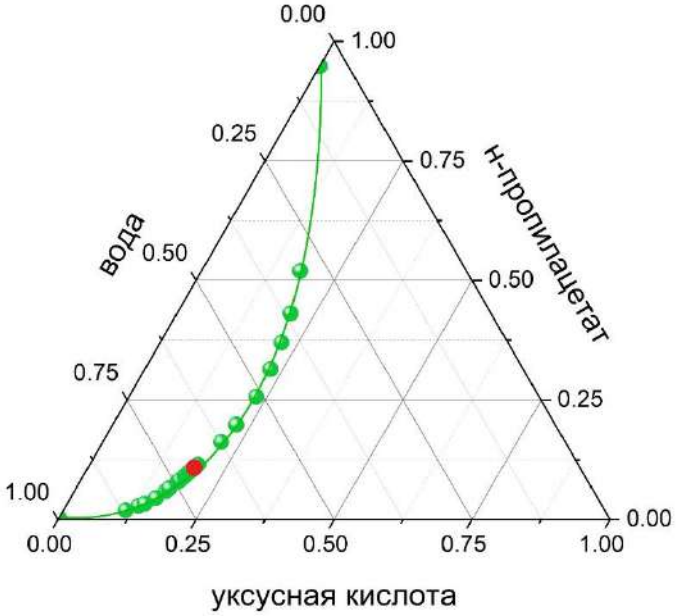

Fig. 3.6.1.2. Solubility region (●) [45, 109] and the critical point (●) [45, 109] in the system acetic acid – n-propyl acetate – water at 293.15 K, mole fractions.

In the n-butyl alcohol – n-butyl acetate – water system (our data [51, 57, 58]), two binary subsystems, n-butyl acetate – water and n-butyl alcohol – n-water, are separated. The separation region in the ternary system has the form of a continuous “band” and there is no critical point in this system, since the heterogeneous region ends on two sides of the concentration triangle belonging to two limitedly miscible binary subsystems (alcohol –

water and ether – water) (Fig. 3.6.1.3.). In general, the study of phase equilibrium in this system has been studied in several works under various experimental conditions [53, 165–167].

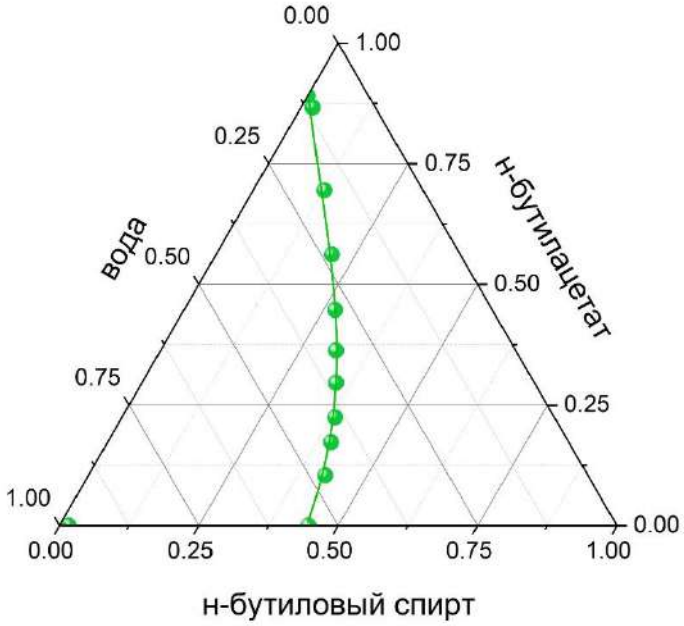

Fig. 3.6.1.3. The stratification region limited by the solubility points (●) [57], in the system n-butyl alcohol – n-butyl acetate – water at 328.15 K, mole fractions.

The ternary system acetic acid – n-butyl acetate – water includes only one stratified binary subsystem (n-butyl acetate – water), therefore the solubility curve has (Fig. 3.6.1.4.) a similarity with the binodal curve in the system acetic acid – n-propyl acetate – water. The phase behavior of the system has been studied quite well [53, 166, 168-171]. The results of the study of this system have also been published in our works [51, 57, 104].

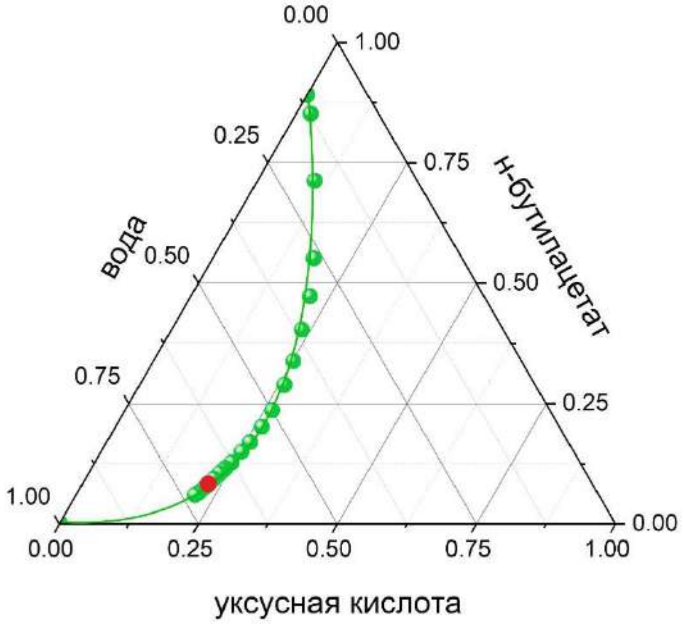

Fig. 3.6.1.4. Solubility (●) [57] and the critical point (●) [57] in the system acetic acid – n-butyl acetate – water at 328.15 K, mole fractions.

Due to the limited miscibility of n-butyl alcohol and water, the acetic acid – n-butyl alcohol – water system also has one critical point. The results presented in the figures of the experimental part and here (Fig. 3.6.1.5) are given in the works [51, 57, 58] published by us. The study of liquid-liquid equilibrium was also carried out by other authors [53, 166, 172, 173], including under other experimental conditions.

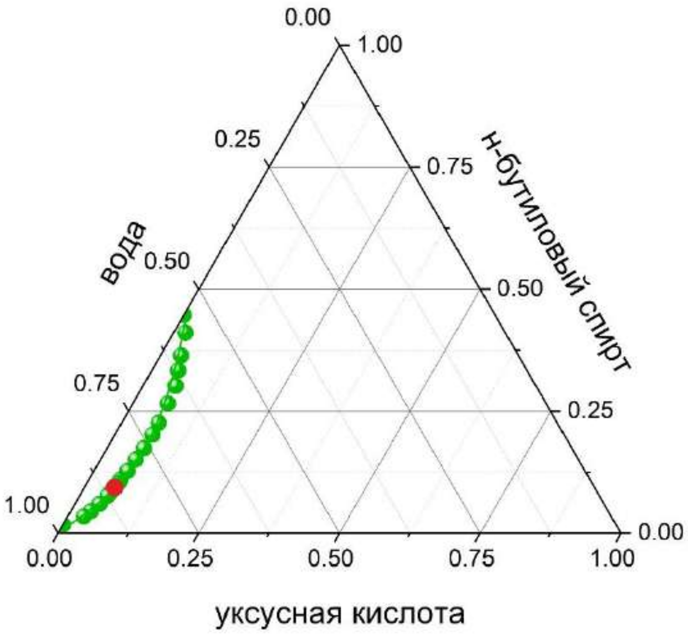

Fig. 3.6.1.5. Solubility (●) [57] and the critical point (●) [57] in the system acetic acid – n-butyl alcohol – water at 328.15 K, mole fractions.

As in the case of the n-butyl alcohol – n-butyl acetate – water mixture, the n-amyl alcohol – n-amyl acetate – water system does not have a critical point, since the stratification region of this system in the concentration space ends at two binary subsystems, namely, n-amyl acetate – water and n-amyl alcohol – water. The system has not been studied previously. To construct the phase diagram (Fig. 3.6.1.6.), data from our studies were used [61, 62, 110].

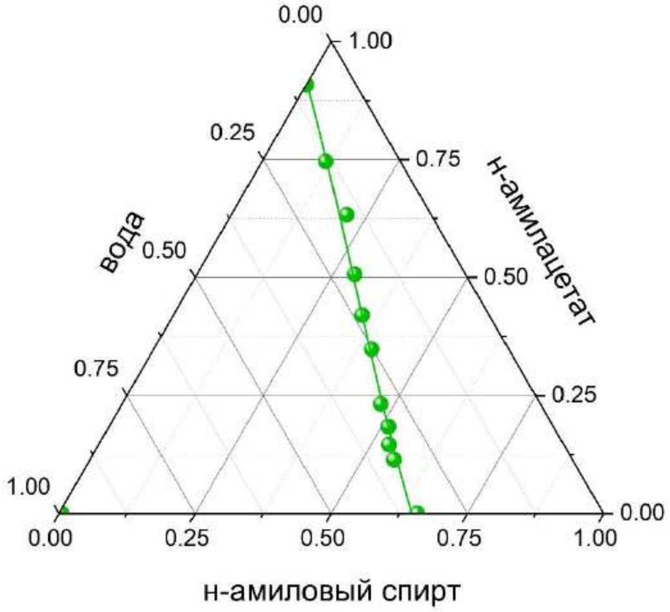

Fig. 3.6.1.6. The stratification region limited by the solubility points (●) [110], in the system n-amyl alcohol – n-amyl acetate – water at 303.15 K, mole fractions.

In the literature, the results of a study of liquid-liquid phase equilibrium for the acetic acid – n-amyl acetate – water system are given in [174]. The system has one binary subsystem with limited miscibility of the components (n-amyl acetate and water). It has a critical point (Fig. 3.6.1.7.). The shape of the binodal curve is similar to the solubility curve, for example, in the acetic acid – n-butyl acetate – water mixture. Data on the compositions of the coexisting phases, solubility and critical states are published in [61–63, 110].

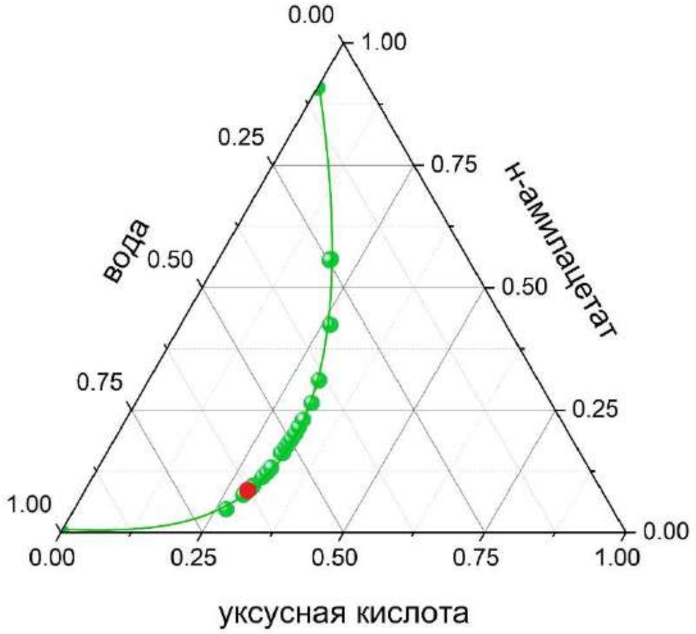

Fig. 3.6.1.7. Solubility (●) [110] and the critical point (●) [110] n the system acetic acid – n-amyl acetate – water at 303.15 K, mole fractions.

For the mixture acetic acid – n-amyl alcohol – water, there are more data in the literature than for the previous system [175, 176]. None of the cited articles show the compositions of the critical phases. The system is heterogeneous under certain conditions, since n-amyl alcohol and water are limitedly miscible with each other. The system has one critical point

(Fig. 3.6.1.8.). The results of the study of the phase behavior of this mixture are presented in our published works [61-63, 110].

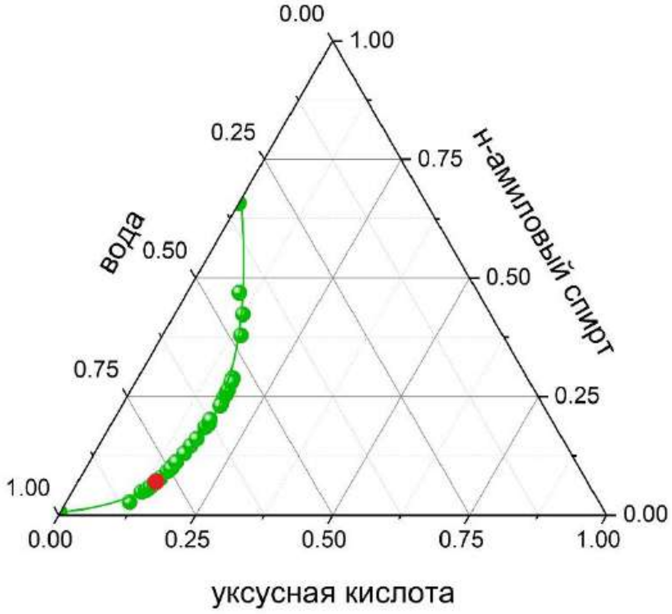

Fig. 3.6.1.8. Solubility (●) [110] and the critical point (●) [110] in the system acetic acid – n-amyl alcohol – water at 303.15 K, mole fractions.

The ethyl alcohol – ethyl propionate – water system was studied at three temperatures and atmospheric pressure [67, 76]. Ethyl propionate, similar to ethyl acetate, is limitedly miscible with water under the given conditions, so stratification is observed in the system as a whole. Critical phenomena and solubility were also studied in [177] at another temperature. Fig. 3.6.1.9 shows the phase diagram constructed according to the data in [67].

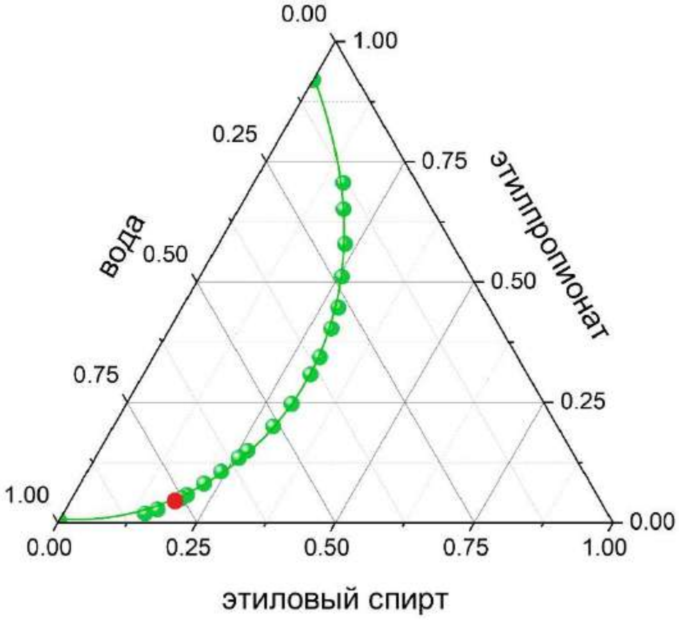

Fig. 3.6.1.9. The stratification region limited by the solubility points (●) [67] and the critical point (●) [67], in the system ethyl alcohol – ethyl propionate – water at 303.15 K, mole fractions.

The propionic acid – ethyl propionate – water system was previously investigated in [71]. The solubility compositions and the compositions of the critical phases are given in our published works [67, 76]. Fig. 3.6.1.10 shows a binodal curve with one critical point. The course of the binodal curve is similar to the course of the solubility curve, for example, in the acetic acid – n-propyl acetate – water system.

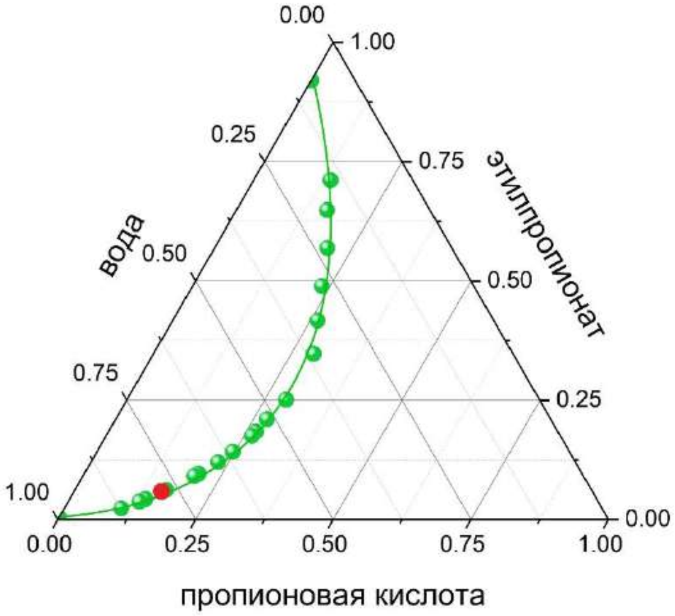

Fig. 3.6.1.10. Solubility (●) [67] and the critical point (●) [67] in the propionic acid – ethyl propionate – water system at 303.15 K, mole fractions.

The results of the titrimetric method for studying solubility in the n-propyl alcohol – n-propyl propionate – water system are presented in [83, 84]. The critical compositions, solubility data and liquid-liquid ratios obtained by us and published in [85, 86] are presented in Fig. 3.6.1.11.

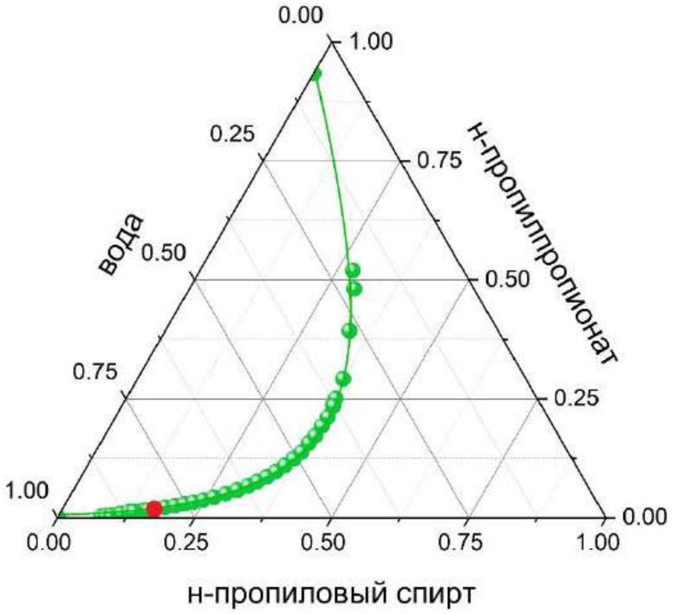

Fig. 3.6.1.11. Solubility (●) [86] and the critical point (●) [86] in the system n-propyl alcohol – n-propyl propionate – water at 303.15 K, mole fractions.

The propionic acid – n-propyl propionate – water system has not been studied previously. All data obtained for this mixture were published by us for the first time in [85, 86]. The shape of the binodal curve (Fig. 3.6.1.12) is similar to the shape of the solubility curve, for example, in the acetic acid – n-butyl acetate – water system (Fig. 3.6.1.4).

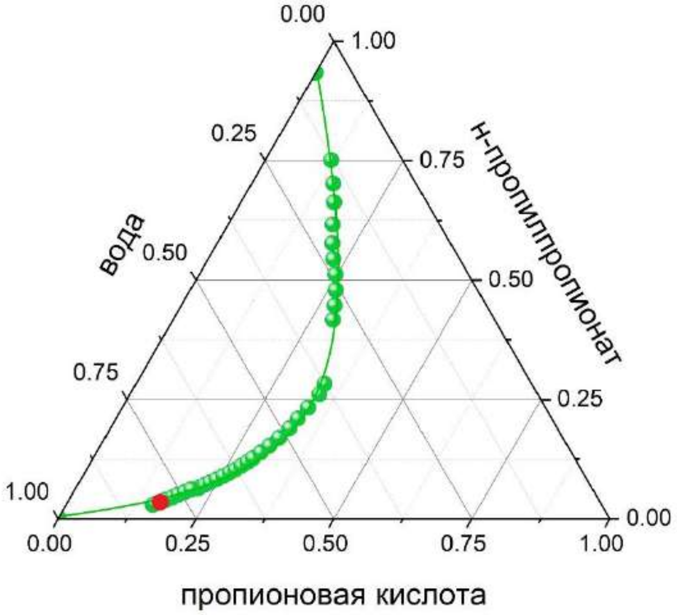

Fig. 3.6.1.12. Solubility (●) [86] and the critical point (●) [86] in the system propionic acid – n-propyl propionate – water at 303.15 K, mole fractions.

The only available data, presented earlier in [89], relate to the study of liquid-liquid-vapour equilibrium in the n-butyl alcohol – n-butyl propionate – water system. We have published the results of a study of liquid-liquid equilibrium and solubility [87, 91]. The system does not have a critical point due to the presence of two binary limitedly miscible subsystems (n-butyl alcohol – water and n-butyl propionate – water). Thus, a continuous heterogeneous region is formed in the concentration triangle, resting on its edges, which correspond to the indicated binary subsystems (Fig. 3.6.1.13).

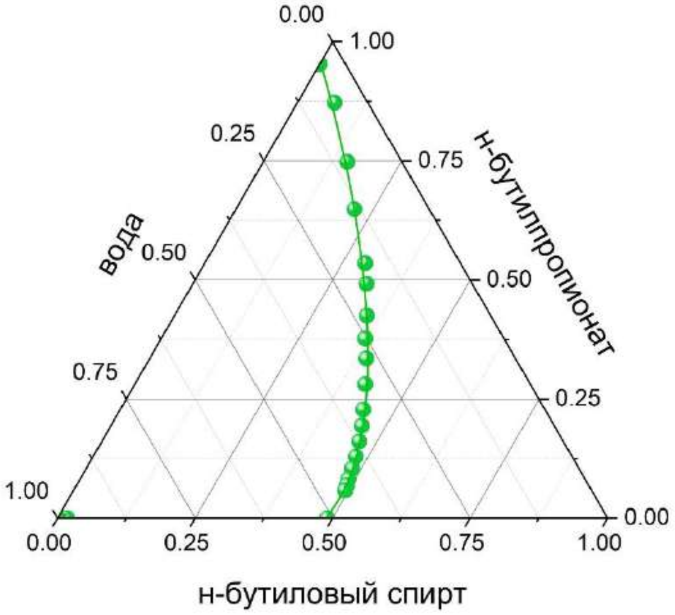

Fig. 3.6.1.13. Solubility and binary liquid-liquid compositions (●) [91] in the system n-butyl alcohol – n-butyl propionate – water at 293.15 K, mole fractions.

For the propionic acid – n-butyl alcohol – water system, there is previously published information in the literature on the course of the solubility curve under various conditions [178–181]. The binodal curve passes through the concentration space, with the ends of this curve resting on the binary subsystem (n-butyl alcohol – water), the components of which are limitedly miscible with each other. The phase diagram shown in Fig. 3.6.1.14 is constructed based on the results of our published works [87, 91].

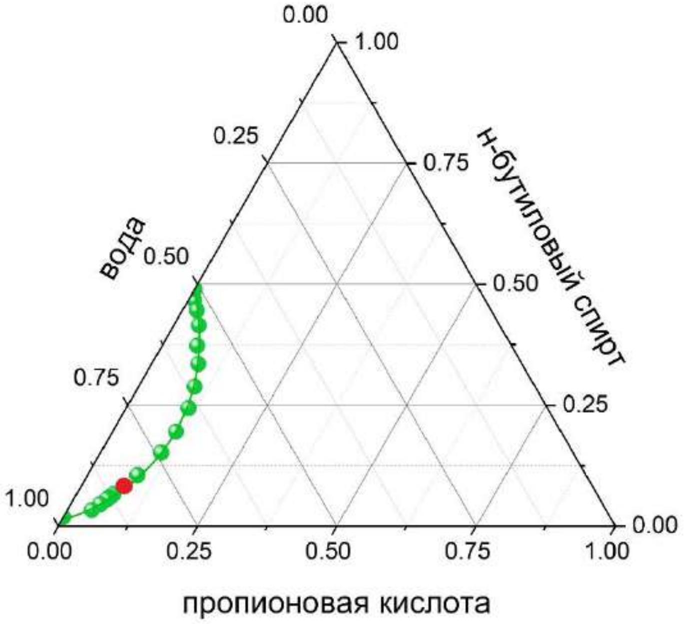

Fig. 3.6.1.14. Solubility (●) [91] and the critical point (●) [91] in the system propionic acid – n-butyl alcohol – water at 293.15 K, mole fractions.

The compositions of the coexisting phases for the propionic acid – n-butyl propionate – water system were previously published in [74] at the boiling temperatures of these components. The mixture has one critical composition (Fig. 3.6.1.15). Detailed results of the solubility study in this system were published by us in [87, 91].

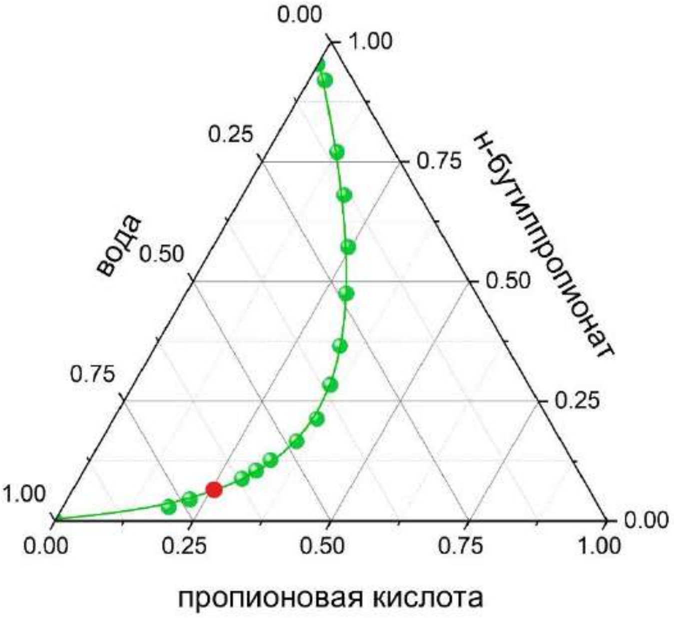

Fig. 3.6.1.15. Solubility (●) [91] and the critical point (●) [91] in the propionic acid – n-butyl propionate – water system at 293.15 K, mole fractions.

For the methyl alcohol – methyl oleate – water system, there is information in the literature on the compositions of the coexisting phases, including the critical composition [94]. Fig. 3.6.1.16 shows the insolubility region in this system, which occupies almost the entire concentration space in the Gibbs-Rosebohm triangle. The results of our study also contain information on the composition of the critical point [92].

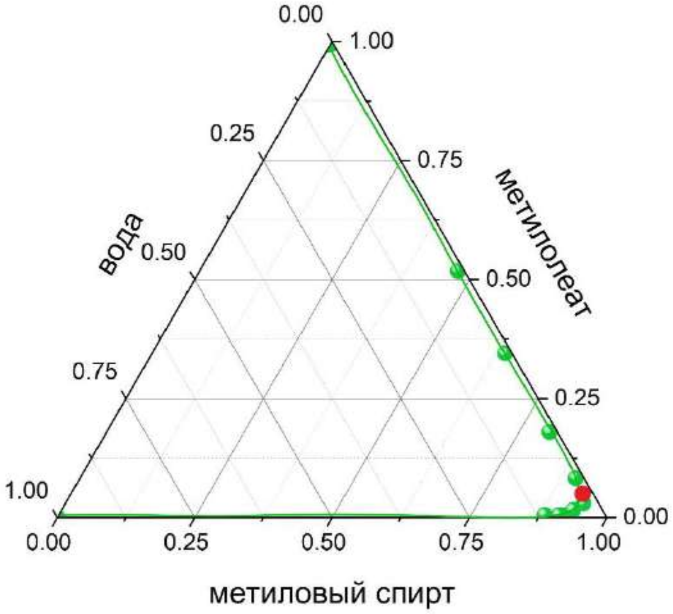

Fig. 3.6.1.16. Solubility, liquid-liquid phase equilibrium compositions (●) [92] and the critical point (●) [92] in the system methyl alcohol – methyl oleate – water at 303.15 K, mole fractions.

The oleic acid – methyl oleate – water system has not been studied previously. Due to the limited solubility of the two binary mixtures in this system (methyl oleate – water and oleic acid – water), the three-component system has two binodal curves that limit the insolubility region in the concentration space (Fig. 3.6.1.17). Thus, critical states are not observed in the oleic acid – methyl oleate – water system. The heterogeneity region shown in Fig. 3.6.1.17 is constructed based on the liquid-liquid equilibrium data we obtained and, as can be seen from the phase diagram, occupies virtually the entire concentration space [92].

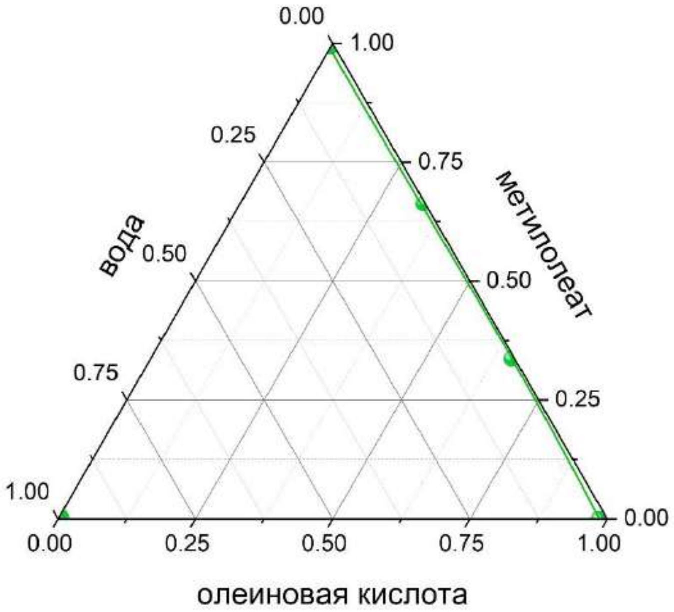

Fig. 3.6.1.17. Liquid-liquid phase equilibrium compositions (●) [92] in the oleic acid – methyl oleate – water system at 303.15 K, mole fractions.

Like the methyl alcohol – methyl oleate – water system, the three-component mixture oleic acid – methyl alcohol – water also has one critical composition under given conditions (Fig. 3.6.1.18) [92]. But, as for the previous system, there are no literature data on solubility.

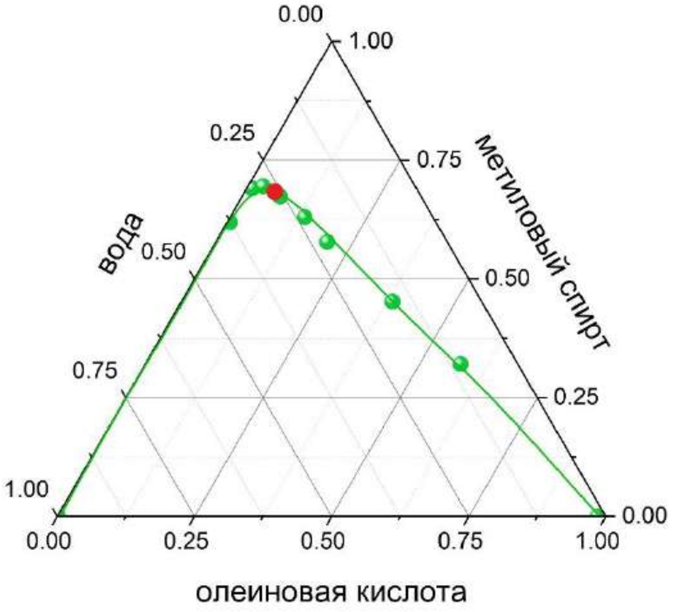

Fig. 3.6.1.18. Liquid-liquid phase equilibrium compositions, solubility (●) [92] and the critical point (●) [92] in the system oleic acid – methyl alcohol – water at 303.15 K, mole fractions.

3.6.2. Critical states and critical surfaces in quaternary systems

As noted above, generalization of the results of Section 3.2 to quaternary systems leads to rather cumbersome equations, despite the reduction in the number of variables. Therefore, for systems of four substances, it is advisable to limit ourselves to classical relations [122, 126]. Below, as in the previous section, we will give examples of the experimental results we obtained, with a brief discussion.

When analyzing the stratification of condensed phases, the influence of pressure, as always, can be neglected. In addition, all our data were obtained for isothermal conditions (T = const), so the first equation of the critical state can be represented through the derivatives of the molar Gibbs energy at T, P = const:

$$D = \begin{vmatrix} \frac{\partial^2 g}{\partial x_1^2} & \frac{\partial^2 g}{\partial x_1 \partial x_2} & \frac{\partial^2 g}{\partial x_1 \partial x_3} \\ \frac{\partial^2 g}{\partial x_2 \partial x_1} & \frac{\partial^2 g}{\partial x_2^2} & \frac{\partial^2 g}{\partial x_2 \partial x_3} \\ \frac{\partial^2 g}{\partial x_3 \partial x_1} & \frac{\partial^2 g}{\partial x_3 \partial x_2} & \frac{\partial^2 g}{\partial x_3^2} \end{vmatrix} =$$

$$= \left[\frac{\partial}{\partial x_1}\left(\frac{\partial g}{\partial x_1}\right)\right]_{x_2,x_3} \cdot \left[\frac{\partial}{\partial x_2}\left(\frac{\partial g}{\partial x_2}\right)\right]_{\left(\frac{\partial g}{\partial x_1}\right),x_3} \cdot \left[\frac{\partial}{\partial x_3}\left(\frac{\partial g}{\partial x_3}\right)\right]_{\left(\frac{\partial g}{\partial x_1}\right),\left(\frac{\partial g}{\partial x_2}\right)} = 0 \quad (3.6.2.1)$$

Relation (3.6.2.1) includes alternative equations of the critical phase (and spinodal), which are identical in physical meaning and can be considered separately: the equality to zero of the Hessian or the product of derivatives. We write the second equation of the critical state only in matrix form:

$$\begin{vmatrix} \frac{\partial^2 g}{\partial x_1^2} & \frac{\partial^2 g}{\partial x_1 \partial x_2} & \frac{\partial^2 g}{\partial x_1 \partial x_3} \\ \frac{\partial^2 g}{\partial x_2 \partial x_1} & \frac{\partial^2 g}{\partial x_2^2} & \frac{\partial^2 g}{\partial x_2 \partial x_3} \\ \frac{\partial D}{\partial x_1} & \frac{\partial D}{\partial x_2} & \frac{\partial D}{\partial x_3} \end{vmatrix} = 0 \quad . \qquad (3.6.2.2)$$

Thus, the critical state in the quaternary system under isothermal-isobaric conditions corresponds to the curve in the concentration tetrahedron. Note that both equations of the critical state are presented, as in other studies, under the assumption of the possibility of neglecting infinitesimals above the second order of smallness (this is the approach adopted in classical studies [122, 126, 127]). This does not seem entirely correct, since the analysis of the stability of the critical state requires the use of infinitesimals of higher orders. In the present work, we leave this problem aside, since it requires a separate study.

Fig. 3.6.2.1 shows the critical curve in the acetic acid – n-propyl alcohol – n-propyl acetate – water system at T = 293.15 K in the concentration tetrahedron [45, 107, 109]. For clarity, the figure also shows the location of the binodal surface. For other temperatures, the corresponding diagrams were presented earlier (in the experimental section).

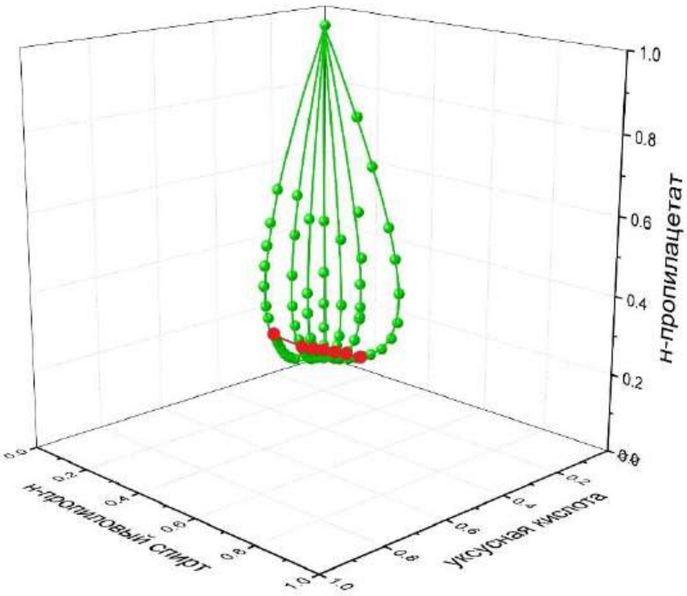

Fig. 3.6.2.1. Solubility surface and critical curve [45, 107, 109] in the acetic acid – n-propyl alcohol – n-propyl acetate – water system at T=293.15 K, mole fractions.

The type of critical curves for the systems propionic acid – ethyl alcohol – ethyl propionate – water, propionic acid – n-propyl alcohol – n-propyl propionate – water, is similar: the critical curve connects two critical points in the ternary subsystems, alcohol – ether – water and acid – ether – water. In the systems acetic acid – n-butyl alcohol – n-butyl acetate – water, acetic acid – n-amyl alcohol – n-amyl acetate – water, propionic acid – n-butyl alcohol – n-butyl propionate – water and oleic acid – methyl alcohol – methyl oleate – water, two binary subsystems are stratified, therefore the appearance of the binodal surface is different for them, and the critical curve also connects two critical points belonging to the subsystems alcohol – ether – water and acid – ether – water (for example, Fig. 3.6.2.2).

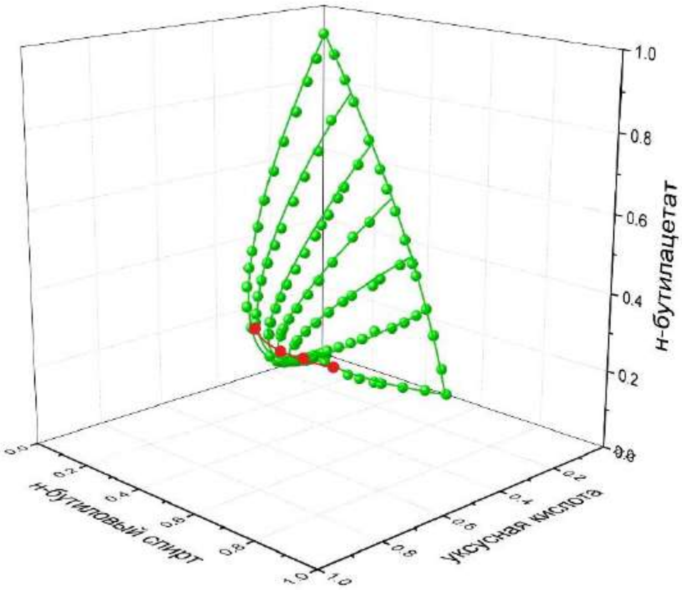

Fig. 3.6.2.2. Binodal surface and critical curve [58] in the system acetic acid – n-butyl alcohol – n-butyl acetate – water at T=308.15 K, mole fractions.

In the case of mixtures involving n-butyl acetate, n-amyl acetate and n-butyl propionate, the presence of a heterogeneous region in three ternary subsystems is associated with stratification not only in the water-ether system, but also in the water-alcohol binary system. In the alcohol-ether-water ternary system, the liquid-liquid equilibrium region, as already indicated, has the form of a strip due to the limited miscibility of water with alcohol and water with ether. For the system with methyl oleate, the heterogeneous region in the acid-ether-water mixture, which has the form of a strip, appears due to the limited solubility of the acid with water and the ether with water. Accordingly, there is no critical point in ternary systems including two binary immiscible subsystems, and the critical curve in the concentration space (composition tetrahedron) is located differently than in other quaternary systems. In other words, in the two types of the listed studied systems, the shapes of the solubility surface differ from each other. All these surfaces can be identified with a segment of an elliptical toroid. In the case of mixtures involving n-propyl acetate, ethyl propionate and n-propyl propionate, the segment has two "bases", while in the case of systems involving n-butyl acetate, n-amyl acetate, n-butyl propionate and methyl oleate, such a segment has three bases.

In most cases, we obtained data on critical curves for different temperatures. Obviously, the set of these curves allows us to construct a polythermal critical surface formed by critical points for different temperatures. Figure 3.6.2.3 shows the critical surface in the acetic acid – n-propyl alcohol – n-propyl acetate – water system at five temperatures: 293.15, 303.15, 313.15, 323.15 and 333.15 K [41]. To our knowledge, data on critical surfaces in multicomponent systems were obtained for the first time in our works. Moreover, similar data have not been published by other authors to date.

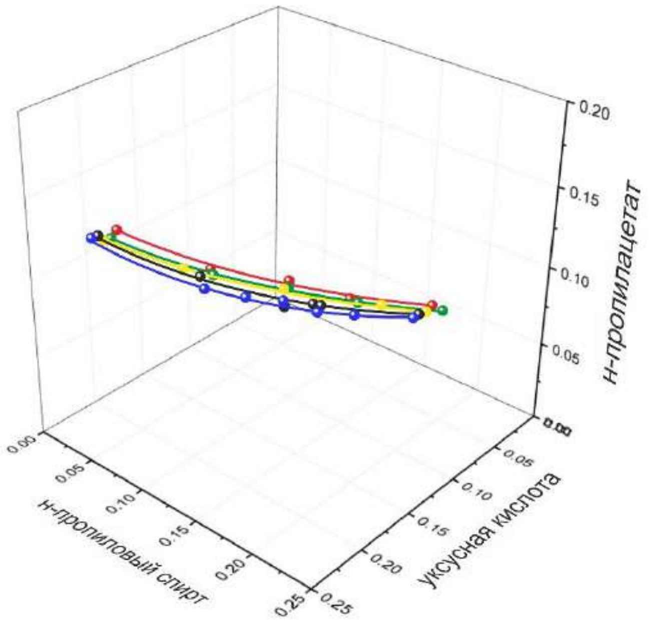

Fig. 3.6.2.3. The critical surface in the system acetic acid – n-propyl alcohol – n-propyl acetate – water at temperatures of 293.15 (● [41]), 303.15 (● [41]), 313.15 (● [42]), 323.15 (●[41]) and 333.15 K (● [41]), mole fractions.

In the article [118] the data on critical surfaces of some pure organic compounds were presented: the critical states of liquid vapor in the coordinates "temperature - pressure - molar volume" were considered. The article also proposed empirical equations for the indicated surfaces. The possibilities of applying these equations to binary systems were considered, among other things. Nevertheless, in this work and some other studies, for example, [182, 183], the authors did not consider critical surfaces in quaternary systems. Some attempts to present the critical plane equation in analytical form, for example, in the article [118], are reduced to empirical (in fact, approximation) equations, which do not have sufficient, either fundamental or practical significance. Thermodynamic relations (3.6.2.1) and (3.6.2.2), which are the equations of critical surfaces in quaternary systems, can certainly be the basis for the analysis of the topology of the indicated surfaces. At present, such processing of arrays of experimental data on the critical properties of multicomponent systems, even with the use of thermodynamic models, is associated with rather labor-intensive calculations and cumbersome equations for analytical representation.

3.6.3. Chemically equilibrium critical phases

Chemically equilibrium critical phases are formed as a result of the intersection of chemical equilibrium surfaces and critical manifolds. Fig. 3.5.4 (section 3.5) qualitatively presents one of the examples of the result of such an intersection, according to the experimental data of this work. The figure also shows the critical curve of liquid-liquid equilibrium, it is obvious that only two critical points C_1, C_2 – at the intersection of the surfaces under consideration – correspond to chemically equilibrium states at a certain temperature.

The critical curves of liquid–liquid equilibrium are additional singularities that are important for characterizing the structure of diagrams of multicomponent systems. Based on data for several temperatures, a set of critical curves belonging to a polythermal critical surface can be constructed. Fig. 3.6.2.3 and Fig. 3.6.3.1 – 3.6.3.3 show such critical surfaces for four quaternary systems.

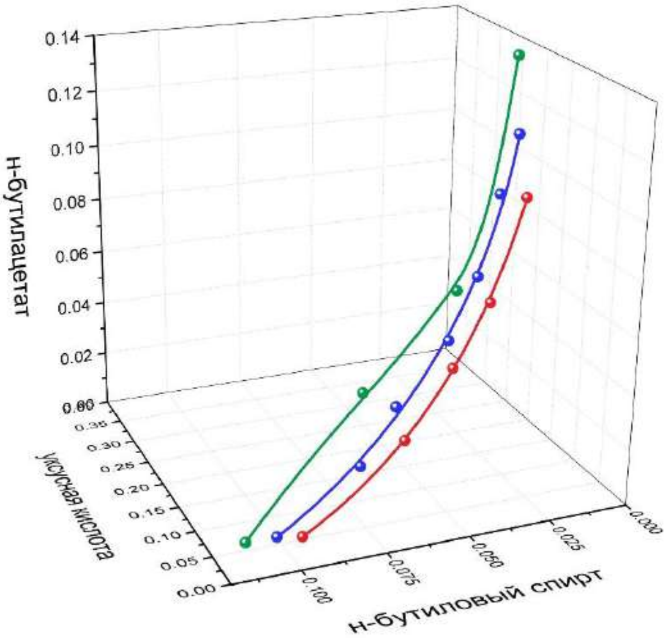

Fig. 3.6.3.1. The critical surface in the system acetic acid – n-butyl alcohol – n-butyl acetate – water at temperatures 308.15 (●[58]), 318.15 (● [51]) and 328.15 К (● [57]), mole fractions.

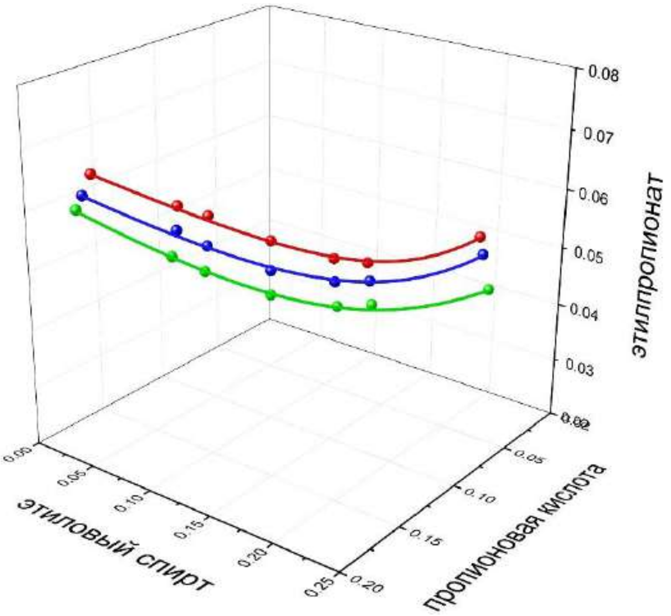

Fig. 3.6.3.2. The critical surface in the system propionic acid – ethyl alcohol – ethyl propionate – water at temperatures 293.15 (●), 303.15 (●) and 313.15 К (●) [67], mole fractions.

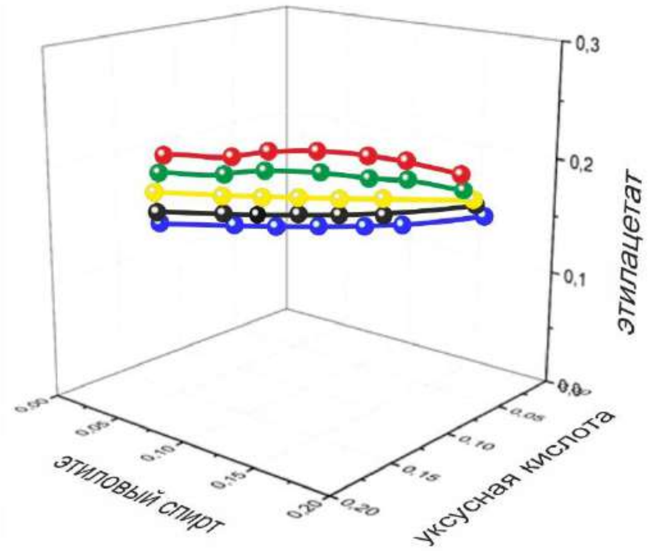

Fig. 3.6.3.3. The critical surface in the system acetic acid – ethyl alcohol – ethyl acetate – water at temperatures 293.15 (● [34]), 303.15 (● [33]), 313.15 (● [33]), 323.15 (●[29]) and 333.15 K (● [29]), mole fractions.

Despite the similar appearance of the polythermal critical surfaces, it is in the systems acetic acid – n-propyl alcohol – n-propyl acetate – water (Fig. 3.6.2.3), acetic acid – n-butyl alcohol – n-butyl acetate – water (Fig. 3.6.3.1) and propionic acid – ethyl alcohol – ethyl propionate – water (Fig. 3.6.3.2) that the critical curves intersect the regions of chemical equilibrium at all temperatures. On each curve in the examples of systems given by us there are two points corresponding to chemically equilibrium states, and, accordingly, in these systems, according to our experimental data, two chemically equilibrium polythermal critical curves can be presented. For the system acetic acid – ethyl alcohol – ethyl acetate – water (Fig. 3.6.3.3) there is no such intersection. Fig. 3.6.3.4 illustrates critical curves consisting of chemically equilibrium critical points in the acetic acid – n-propyl alcohol – n-propyl acetate – water system [38].

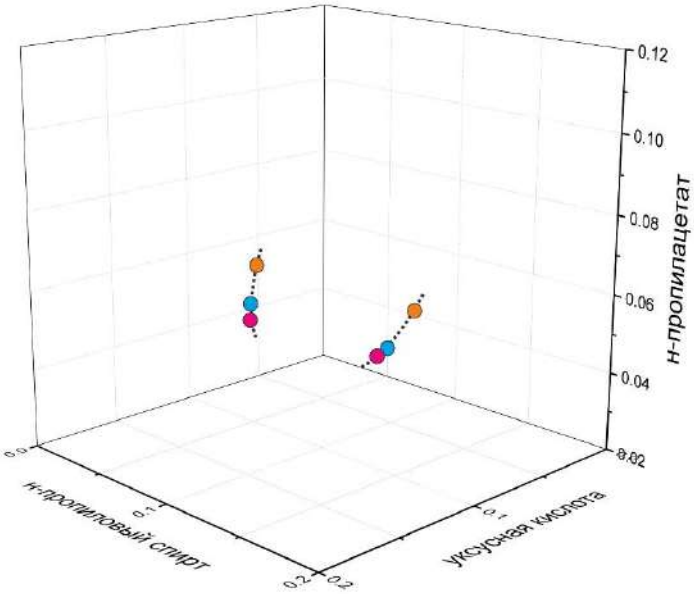

Fig. 3.6.3.4. Critical curves [38] in the system acetic acid – n-propyl alcohol – n-propyl acetate – water, corresponding to chemically equilibrium compositions under polythermal conditions: 293.15 (●), 303.15 (●), 313.15 K (●), mole fractions.

The arrangement of chemically equilibrium critical curves in thermodynamic space must be consistent with equation (3.3.16) and other relations of section 3.3 for the stability boundary of systems in chemical equilibrium. Note that the seemingly simple form of, for example, relation (3.3.16), does not reflect the complexities associated with calculations using this equation. Representation of changes in chemical potentials in analytical form, even with the use of thermodynamic models (model equations), leads to even more cumbersome relations and additional calculation complexities. This is due to the second equation of the critical state. Therefore, in this paper we limit ourselves to presenting experimental data on chemically equilibrium critical phases and stating that these surfaces are described by equations that coincide with the equations of the stability boundaries, i.e., the first equation of the critical state. Chemically equilibrium critical compositions are also present in other studied systems. We have published several such compositions for systems involving n-butyl acetate [59] and n-amyl acetate [63]. In these cases, each of the temperatures studied corresponds to only one chemically equilibrium critical point due to a different shape of the binodal surface in the listed systems, compared to systems involving n-propyl acetate, ethyl propionate and n-propyl propionate (see Section 3.6.2). And for a more visual representation of these critical compositions in the concentration space, it is more convenient to use the square of " -variables" [10] (Section 3.5). Fig. 3.6.3.5 and 3.6.3.6 show the regions of the concentration space in which the intersection of the phase and chemical equilibrium surfaces occurs, resulting in the formation of chemically equilibrium heterogeneous compositions, as well as chemically equilibrium critical phases. All critical surfaces and critical curves for the systems presented in the work, studied by us.

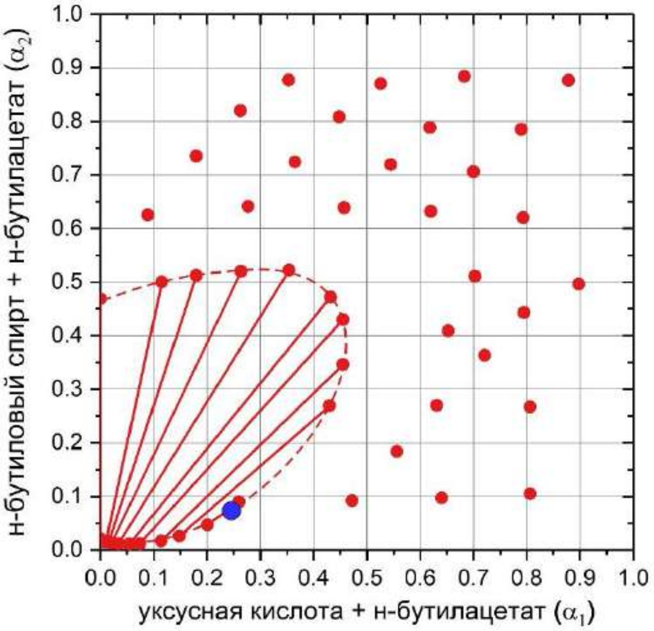

Fig. 3.6.3.5. Square of «α- variables» for the system acetic acid – n-butyl alcohol – n-butyl acetate – water at a temperature 318.15 K [59]: ● – homogeneous chemically equilibrium compositions, ●—● – heterogeneous chemically equilibrium compositions, --- – boundary of the heterogeneity region in a state of chemical equilibrium, ● – chemically equilibrium critical point, mole fractions.

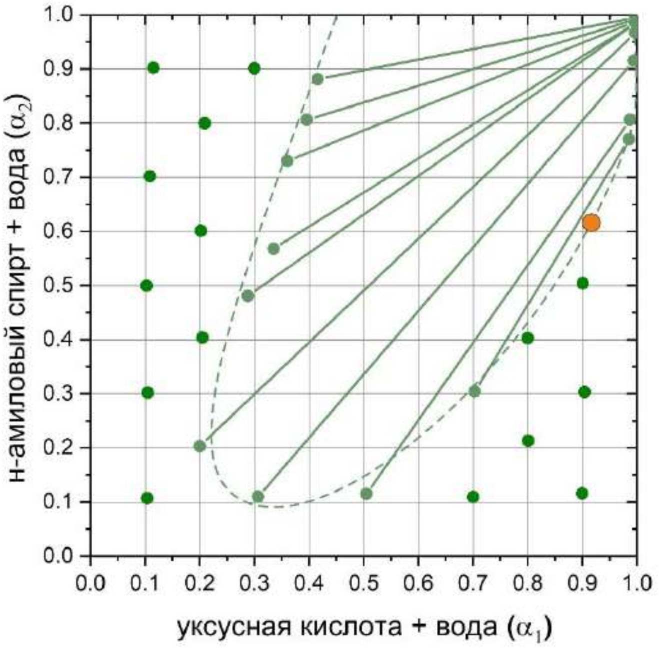

Fig. 3.6.3.6. Square of «α- variables» for the system acetic acid – n-amyl alcohol – n-amyl acetate – water at a temperature 318.15 K [63]: ● – homogeneous chemically equilibrium compositions, ●—● – eterogeneous chemically equilibrium compositions, --- – boundary of the heterogeneity region in a state of chemical equilibrium, ● – chemical equilibrium critical point, mole fractions.

In conclusion, we note that the experimental data on chemically equilibrium critical curves obtained in our work currently have no analogues in the world literature. In further studies, it is advisable to consider these complex issues - chemical processes and chemical equilibrium in a dynamic reaction environment in which continuous nucleation and decay processes of nuclei occur - using experimental methods and calculation apparatus that allow analysis at the molecular level, i.e., not limited to the thermodynamic approach.

KEY FINDINGS

1. The obtained set of experimental results on critical states forms the basis of the database on critical phenomena in multicomponent liquid-phase systems with chemical interaction of the constituent substances.
2. The set of experimental data on chemical equilibrium in systems with reactions of synthesis/hydrolysis of carboxylic acid esters in wide temperature ranges allowed to calculate the thermodynamic and "concentration" constants of chemical equilibrium. The calculations and correlations were performed using the equations of the local composition model (NRTL) and the group model (UNIFAC).
3. The set of new detailed experimental data on solubility and liquid-liquid equilibrium in quaternary systems made it possible to evaluate the features of their phase behavior. Data correlations based on the equation of the local composition model (NRTL) and classical verification methods (Othmer-Tobias, Hand, Marchilla, etc.) confirm the thermodynamic consistency of the results. The results were also processed using the UNIFAC group model. When analyzing the relative positions of binodal surfaces and chemical equilibrium surfaces in the concentration space (composition tetrahedra), important topological patterns were established. In particular, data on chemical equilibrium in the heterogeneous region, i.e. for compositions that correspond to simultaneous chemical and phase equilibria, are of particular interest. The set of corresponding liquid-liquid tie-lines forms ruled surfaces that can be considered as a “unique liquid-liquid reaction surface” similar to “unique reactive liquid-liquid tie-lines” in ternary systems.
4. For the first time, experimental data were obtained on polythermal critical surfaces in multicomponent systems with chemical reactions. These surfaces are an important element of the topological structures of state diagrams of quaternary systems, their representation in three-dimensional concentration space.
5. For the first time, compositions of chemically equilibrium critical points in the concentration space were found, which are formed by the intersection of critical curves and chemical equilibrium surfaces in the composition tetrahedron. 6. The developed approach and the proposed new methodology for theoretical study of the regularities of the structure of state diagrams of systems with chemical interaction of substances in the vicinity of critical points are based on the thermodynamic relationships derived in the work, which are based on the introduction of new variables (analogs of mole fractions). A general equation for the isothermal-isobaric curve of chemical equilibrium in the specified generalized concentration variables for ternary systems is derived. An analysis of the behavior of chemically reacting ternary liquid-liquid systems in the vicinity of critical points of two-phase equilibria is carried out, and the corresponding diagrams are given.
7. New forms of stability conditions for multicomponent systems with chemical interaction of substances are derived, which made it possible to obtain modified spinodal and critical state equations.
8. The obtained data on chemical equilibrium, phase (liquid-liquid) and critical phases, mutual arrangement of the specified manifolds in thermodynamic space are necessary for the scientific organization of processes of separation of industrial and natural mixtures, including components of reactions of synthesis and hydrolysis of esters, combined processes of “synthesis + separation” in chemical technology of obtaining esters of carboxylic acids, biofuel technology and related industrial fields.

LIST OF PUBLISHED WORKS BASED ON THE THESIS

1. Georgii Misikov, Konstantin Zolotovsky, Artemiy Samarov, Igor Prikhodko, Maria Toikka and Alexander Toikka. Chemical Equilibrium in the System Acetic acid − *n*-Amyl Alcohol − *n*-Amyl Acetate − Water at 323.15 K and Atmospheric Pressure: Experimental Data and Equilibrium Constant Estimation // Journal of Chemical & Engineering Data 69 (2024) 1169-1177. Doi: 10.1021/acs.jced.3c00744
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4. Maria Toikka, Alexander Smirnov, Maya Trofimova, Alexandra Golikova, Igor Prikhodko, Artemiy Samarov, and Alexander Toikka. Peculiarities of Chemical Equilibria in Acetic Acid − n-Butyl Alcohol − n-Butyl Acetate − Water System at 318.15 K and 101.3 kPa // Journal of Chemical & Engineering Data 68 (2023) 1145–1153. Doi: 10.1021/acs.jced.3c00009
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9. Misikov G., Toikka M., Samarov A., Toikka A. Phase equilibria liquid-liquid for ternary systems *n*-amyl alcohol – water – (acetic acid, *n*-amyl acetate), *n*-amyl acetate – water – acetic acid at 293.15 K, 303.15 K, 313.15 K and 323.15 K // Fluid Phase Equilibria 552 (2022) 113265. Doi: 10.1016/j.fluid.2021.113265
10. Maya Trofimova, Georgii Misikov, Artemiy Samarov, Igor Prikhodko and Maria Toikka. Solubility in the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water at 293.15 K, 303.15 K, 313.15 K and 323.15 K and atmospheric pressure // The Journal of Chemical Thermodynamics 161 (2021) 106515. Doi: 10.1016/j.jct.2021.106515
11. Alexander Smirnov, Artemiy Samarov, Maria Toikka. Liquid−Liquid Equilibrium, Solubility, and critical states in an acetic acid − *n*-butyl alcohol − *n*-butyl acetate − water system at 328.15 K and 101.3 kPa: Topology of Phase Diagrams and NRTL Modeling // Journal of Chemical & Engineering Data 66 (2021) 1466-1474. Doi: 10.1021/acs.jced.0c01066

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LIST OF ABBREVIATIONS

Mol. fraction. – mole fraction
g - gram
atm – atmosphere
f – system variability
n – number of substances
r – number of phases
k – number of chemical reactions
T – temperature
P – pressure
V, v – volume
μ – chemical potential
m_i – amount of substance i
x_i – amount of substance i
G, g – Gibbs energy
g_{ij} – second derivatives of the molar Gibbs energy
R_i – substance symbol i
v_i – stoichiometric coefficient of a substance i
c_{ji} – real coefficients
$\widetilde{m_i}$ – generalized number of moles of a substance i
$\widetilde{m_j}$ – generalized number of moles of a substance j
$\tilde{\mu}_i$ – generalized chemical potential of a substance i
$\tilde{\mu}_j$ – generalized chemical potential of a substance j
$\widetilde{x_i}$ – mole fraction analogue of a substance i
$\widetilde{x_j}$ – mole fraction analogue of a substance j
S, s – entropy
$\tilde{v}_i$ – analog of the stoichiometric coefficient of a substance i
$\tilde{v}_j$ – analog of the stoichiometric coefficient of a substance j
$O\tilde{x}_1$, $O\tilde{x}_2$ – coordinate axes
$\tilde{g}_{ij}$ – second derivatives of the Gibbs energy of generalized mole fractions
$\tilde{g}_{ij}^{o}$ – second derivatives of the Gibbs energy from the generalized mole fractions in the case of complete degeneration of the stability matrix
α_i – transformed composition variables
U, u – internal energy
r_i – mass of substance i
$'$, $''$ – superscripts for the "original phase" and the phase infinitely close in properties, respectively
X_i – intensive parameter
Y_i – conjugate extensive parameter
A – affinity

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