Phase Behavior of Ternary Hydrothermal Systems – Experiment and Modeling.

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The method of continuous topological transformations and the systematic classification of binary phase diagrams containing the boundary versions of phase diagrams with ternary nonvariant points, were applied to derive the main types of fluid and complete phase diagrams for ternary systems with one volatile component and immiscibility phenomena in two constituent binary subsystems. Some general features of phase behavior in ternary mixtures at sub- and supercritical conditions are formulated using the results of theoretical derivation, available information on hydrothermal phase equilibria and new experimental data for the system $Na_2CO_3 – K_2CO_3 – H_2O$.

1. Introduction

The method of continuous topological transformation of phase diagrams [1, 2] is based on the premise that each type (or topological scheme) of phase diagram can be continuously transformed into another type (with a different set of phase equilibria) through the boundary version of that phase diagram, which has the properties of both neighboring types and contains the equilibria possible only in the systems with the higher numbers of components. It was established for the binary fluid phase diagrams by analytical investigations of various equations of state where the boundary versions with ternary nonvariant points were obtained as the transitions of one type of binary fluid phase diagram into another [3, 4].

Modifications of stable fluid phase equilibria in the presence of a solid phase do not change the type and topological scheme of fluid phase behavior and originate in the boundary versions of binary phase diagram with nonvariant ternary critical points where the solid phase takes part in equilibria. As a result of such modification, a part of fluid equilibria (for instance, a part of immiscibility regions and/or critical curves) is suppressed by solidification of the nonvolatile component and transforms into the metastable equilibria. The phase diagrams that not only describe the fluid but also any equilibria between liquid, gas and/or solid phases in a wide range of temperatures and pressures are referred to as complete phase diagrams.

The systematic classification of complete phase diagrams for binary systems, shown in Fig. 1, was derived using the method of continuous topological transformation, consists of four horizontal rows (**a, b, c, d**) and three vertical columns (**1**, **1'(1'')**, **2**) and is complete and exhaustive within the framework of the definite limitations [2].

Complete phase diagrams in the row **a** are characterized by a fluid phase behavior without liquid-liquid immiscibility phenomena. A limited immiscibility region, where the three-phase equilibrium L_1-L_2-G ends at the critical points N (L_1=L_2-G) both at high and low temperatures (in stable or metastable conditions), is a permanent element of complete phase diagrams in the row **b**. Two three-phase immiscibility regions L_1-L_2-G of different nature are the constituents of complete phase diagrams in the row **c**. Three-phase immiscibility region with two critical endpoints N (L_1=L_2-G) and R (L_1=G-L_2) of different nature can be found in any complete phase diagrams of the row **d**. Three horizontal rows **b**, **c** and **d** consist of two lines of phase diagrams because there are the experimental examples for phase diagrams of the both lines in the row **d**.

Three vertical columns (right, central, and left) of complete phase diagrams reflect the various features of solid-fluid equilibria. The complete phase diagrams, which show four main types of fluid phase behavior and lack critical or immiscibility phenomena in solid-saturated solutions, are found in the left column. The central and right columns contain diagrams with nonvariant points where critical phenomena occur in equilibrium with a solid phase. So-called "supercritical fluid" and "supercritical fluid – solid" equilibria are absent in the diagrams from central column, but they appear in the diagrams of type **2** from the right column. The boundary versions of binary phase diagrams separate the neighboring types of complete phase diagrams.
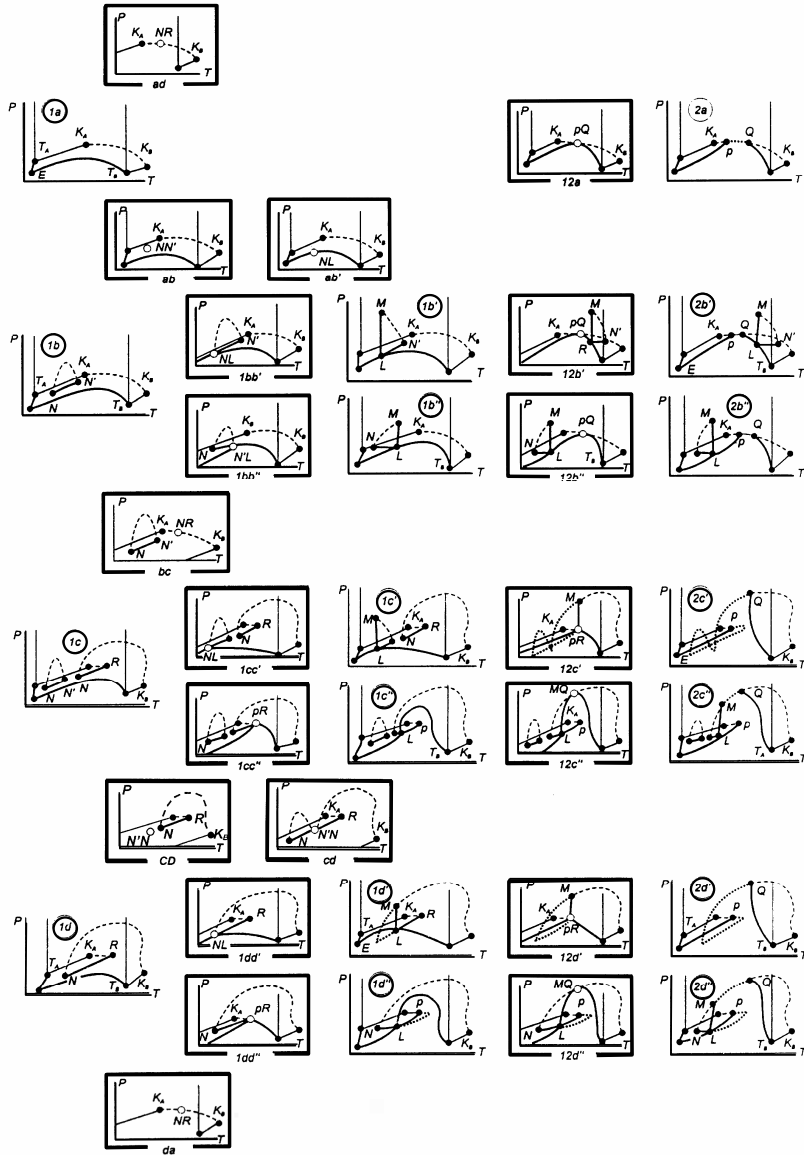
Figure 1. Systematic classification of binary complete phase diagrams (P-T projections).

The diagrams shown in frames are the boundary versions with ternary nonvariant points. Filled dots are nonvariant points in one- and two-component systems (T_A, T_B and K_A, K_B – triple (L-G-S) and critical (L=G) points of pure components A and B; eutectic point E (L-G-S_A-S_B); L (L_1-L_2-G-S_B); critical endpoints: N(N') (L_1=L_2-G), R (L_1=G-L_2), p (L=G-S), Q (L=G-S or L_1=L_2-S), M (L_1=L_2-S). Open dots are nonvariant equilibria of ternary systems (NL(N'L) (L_1=L_2-G-S); pR (L_1=G-L_2-S); double critical endpoints N'N (L_1=L_2-G), pQ (L=G-S), MQ (L_1=L_2-S); tricritical point NR (L_1=L_2=G)) in the boundary versions of phase diagram (in frames). Thin lines are monovariant equilibria L-G and L-S of pure components A and B; dashed lines are critical curves L=G and L_1=L_2. Heavy lines are monovariant curves (non-critical) of binary system; dotted lines are the metastable parts of monovariant curves in binary systems.

2. Derivation of Fluid and Complete Ternary Phase Diagrams

The phase diagrams of constituent binary subsystems determine the major features of ternary phase diagrams since all binary equilibria spread into the three-component region of composition and take part in a generation of ternary phase behavior. Therefore the main types of phase behavior of binary subsystems can be used for preliminary systematization and designation of the various classes of ternary water-salt systems.

If the phase behavior of the constituent binary subsystems is known, the task of constructing a topological scheme for a ternary system translates into the finding of new nonvariant equilibria. These equilibria result from the intersection of monovariant curves originated at nonvariant points of the constituent binary subsystems. While passing from one binary subsystem to another, the phase diagrams of the binary subsystems must undergo continuous topological transformations in the three-component region of composition. This process may be imagined as a continuous phase diagram transformation of quasi-binary sections of the ternary system with a constant volatile component (water) and continuously changing non-volatile component (from one salt component to another). This constitutes so-called "quasi-binary approach" to the ternary phase equilibria.
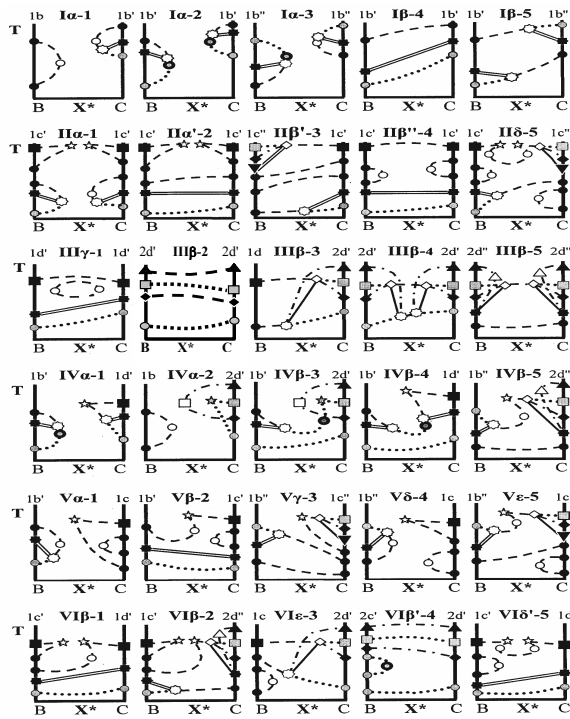

Figure 2 T-X* projections (schemes) of some complete phase diagrams for ternary systems with one volatile component (A) and immiscibility phenomena in two binary subsystems (A – B, A – C). X* denotes the relative amounts of the non-volatile components (B, C) in ternary solutions (X*=$X_B/(X_B+X_C)$), where $X_{B,C} = m_{B,C}/(m_A + m_B + m_C)$.

Symbols for stable and metastable (m/s) nonvariant points and monovariant lines:

▲ - Q (($L_1=L_2$-S))   ⬜ (gray) - R **m/s** (L_1=G-L_2)   □ - pQ (L=G-S)
■ - R (L_1=G-L_2)   ◯ (gray) - N **m/s** ($L_1=L_2$-G)   ○ - N'N ($L_1=L_2$-G)
● - N ($L_1=L_2$-G)   ⬤ - N'N **m/s** ($L_1=L_2$-G)   ⬠ - NL ($L_1=L_2$-G-S)
◆ - p (L=G-S)   ☆ - NR **m/s** (L_1=G=L_2)   ◇ - pR (L=G-L_2-S)
▼ - L (L_1-L_2-G-S)   ★ - NR ($L_1=L_2$=G)   △ - MQ ($L_1=L_2$-S)
✿ - L (L_1-L_2-G-S) + M ($L_1=L_2$-S)   ═══ - (L_1-L_2-G-S) + ($L_1=L_2$-S)
──── - (L_1-L_2-G-S)   ‒ ‒ ‒ - ($L_1=L_2$-G) or (L_1=G-L_2)
‒·‒· - ($L_1=L_2$-S) or (L=G-S)   ········· - **m/s** ($L_1=L_2$-G) or (L_1=G-L_2)

If the phase diagrams of the binary subsystems are present in Figure 1, then all the steps of the topological transformation between these diagrams are also shown there as a set of phase diagrams (including the boundary versions, which show the ternary nonvariant points) corresponding to the quasi-binary sections [2].

A more systematic approach to the global phase behavior of ternary systems should start from a derivation of the main types of ternary fluid phase diagrams and following consideration of how these phase diagrams are modified by the presence of the solid phase of the nonvolatile components. A description of this approach is available elsewhere [2, 5]. Here we can give only an outline of some results that were gained from the analysis of fluid and complete phase diagrams for the ternary systems with one volatile and two nonvolatile components where two binary subsystems with volatile component are complicated by immiscibility phenomena and the third binary subsystem belongs to type **1a**.

There are 6 major classes of such ternary fluid mixtures that can be referred to as ternary class **I** with the following combination of constituting binary subsystems (**1a-1b-1b**), ternary class **II** - (**1a-1c-1c**), ternary class **III** - (**1a-1d-1d**), ternary class **IV** - (**1a-1b-1d**), ternary class **V** - (**1a-1b-1c**) and ternary class **VI** - (**1a-1c-1d**).

The derivation by the method of continuous topological transformation was made on the assumption that the immiscibility regions spread from two binary subsystems can either merge in the three-component range of composition or be separated by a miscibility region. The later case is especially important since it illustrates the phase behavior in another classes of ternary systems, where only one of the consistuent binary subsystems with volatile component is complicated by liquid-liquid immiscibility (**1a-1b-1a**), (**1a-1c-1a**), (**1a-1d-1a**). The result of derivation is 39 schemes of ternary fluid phase diagrams [2].

Until the equilibrium L-G-S intersects the three-phase immiscibility region L_1-L_2-G, the stable fluid phase equilibria are not changed and correspond to the main types of fluid phase diagram. An appearance of equilibrium L_1-L_2-G-S (the nonvariant point L in binary systems and the monovariant curve in ternary system) leads to transition of a part of immiscibility region into metastable conditions. An increase in temperature of solid phase interference in immiscibility and critical equilibria increases the metastable part of immiscibility region and initiates an appearance of supercritical fluid equilibria and a transition of binary or quasi-binary phase diagrams from type **1** to type **2**.

Figure 2 shows several examples of ternary complete phase diagrams represented as five T-X* projections of ternary phase diagrams for each of six ternary classes **I-VI**, derived in assumptions that the solid phases of nonvolatile components form a continuous solid solution and the temperatures of binary nonvariant points L (L_1-L_2-G-S) and M (L_1=L_2-S) are equal.

The following general regularities of phase behavior in ternary mixtures can be formulated from the analysis of derived ternary phase diagrams, shown in Figure 2:

1. Ternary immiscibility regions spreading from the binary subsystems can either be terminated by nonvariant points and disappear or merge with another immiscibility region. Disappearance of the immiscibility region of type **b** occurs in the double critical endpoint (DCEP) N'N (L_1=L_2-G) or in the nonvariant critical point LN (L_1=L_2-G-S).

The immiscibility region of type **d** ends in the tricritical point (TCP) NR (L_1=L_2=G). The immiscibility region of type **c** can disappear in the TCP NR (L_1=L_2=G) only after continuous transformation into immiscibility region of type **d** through the DCEP N'N (L_1=L_2-G).

In the case of two separated immiscibility regions joining into a single one, two monovariant critical curves of same nature spreading from the different binary subsystems form a single critical locus without new nonvariant points. DCEP N'N (L_1=L_2-G) appears on the critical curves L_1=L_2-G which intersects in the TCP NR (L_1=L_2=G) with the critical curve L_1=G-L_2 spreading from another binary subsystem.

2. The occurrence of two-phase holes L-G (completely bounded by a closed-loop critical curve L_1=L_2-G) in the three-phase immiscibility region was established experimentally for ternary systems with two binary subsystems of type **d** [6]. However it is felt that the two-phase hole could be found in ternary systems with binary subsystems of type **c** and even type **b**.

3. The monovariant curve L-LN (L_1-L_2-G-S) originated in binary subsystem of types **1b'**, **1c'**, or **1d'** is located at temperature range below the temperature of point L. The low-temperature part of ternary three-phase immiscibility region located on the T-X* projection below the curve L-LN is metastable. The monovariant curves L-pR or L-LN (L_1-L_2-G-S) originated in binary subsystems of types **1b''**, **1c''**, or **1d''** are located at higher temperatures than the binary point L and the high-temperature part of ternary three-phase immiscibility region is

metastable in the range of composition (X*) from binary subsystem to ternary critical points LN and pR.

4. Transition from metastable into stable equilibria of a three-phase immiscibility region spreading from binary subsystem of types **2c'** or **2d'** starts from the high-temperature equilibrium pR (L_1=G-L_2-S) and terminates in the low-temperature point LN (L_1=L_2-G-S). The same transition of a three-phase immiscibility region spreading from binary subsystem of types **2c''** or **2d''** is terminated by an appearance of the high-temperature ternary point pR (L_1=G-L_2-S) and the high-pressure DCEP MQ (L_1=L_2-S).

5. If three-phase metastable immiscibility region spreading from the binary subsystem of type **2** disappears in metastable conditions of the ternary system, the DCEP pQ (L=G-S) should appear in stable equilibria.

3. Experimental Results

Some regularities of phase behavior in ternary mixtures formulated in the previous division can be confirmed by the available results of experimental studies obtained with the methods described in [1, 7] for ternary water-salt systems.

Ternary class 1-1-1. If only one of constituting binary water-salt subsystem has the immiscibility phenomena, the ternary system of class **1-1-1** is complicated by three-phase immiscibility region that should disappear in the ternary nonvariant critical point in accordance with the rules formulated in the item 1. The system $Na_2B_4O_7$ – NaCl – H_2O belongs to ternary class **1a-1d-1a** with the binary subsystem $Na_2B_4O_7$ – H_2O of type **1d** [8] and the immiscibility region spreading from this binary subsystem ends in the tricritical point RN (L_1=L_2=G) [8].

Ternary system HgI_2 – PbI_2 – H_2O [9] belongs to ternary class **1b'-1d'-1a**. Two versions of complete phase diagram (**IVα-1** and **IVβ-4**) are shown for such ternary class in Fig. 2. In the both versions of complete phase diagram, the immiscibility region of type **d** (spreading from the subsystem PbI_2 – H_2O) ends in the tricritical point RN. Another immiscibility region of type **b** (spreading from subsystem HgI_2 – H_2O) in the both topological schemes is terminated by the invariant critical point LN (L_1=L_2-G-S) in solid saturated solutions. The distinctive feature of the theoretical schemes lies in the forms of ternary immiscibility regions. The immiscibility regions spreading from two binary subsystems are separated by miscibility region in the case of scheme **IVα-1** but merged into a single ternary immiscibility region in the case of scheme

IVβ-4. However the experimental data do not permit to select the scheme of complete phase diagram for the system HgI_2 – PbI_2 – H_2O because they do not contain any information about the metastable equilibria.

Ternary class 2-2-1. Two types of ternary phase behavior were established theoretically (see schemes **IIIβ-2** and **IIIβ-4** in Fig. 2) for ternary class **2d'-2d'-1a** and in the experimental studies of ternary systems with two binary water-salt subsystems of type **2** complicated with immiscibility phenomena (type **2d'**) [1]. In the first case the three-phase immiscibility region of ternary mixtures is retained in metastable conditions (scheme **IIIβ-2**) at any ratio of salt components including the eutonic solution. Such phase behavior was found in the ternary system $Na_2Si_2O_5$ (Ds) – Na_2SiO_3 (Ms) – H_2O [1] and in several oxides and alumino-silicates systems, where the eutonic solution is terminated by the second critical endpoint (L_1=L_2-S_1-S_2) similar to the solubility curves in the binary subsystems H_2O – $Na_2Si_2O_5$ and H_2O – Na_2SiO_3 that are terminated in the critical endpoints L_1=L_2-S_{Ds} and L_1=L_2-S_{Ms}. Another type of phase behavior (scheme **IIIβ-4**) takes place when the metastable immiscibility region becomes stable in ternary solutions. As a result the joint solubility of two salt components increases drastically, because the immiscibility region separates the eutonic (joint solubility of both salts in water at vapor pressure) and the solubility (solubility of each salt in water at vapor pressure) curves. The temperature coefficient of solubility in eutonic solutions becomes positive and critical phenomena in these solutions saturated with two solid phases are absent. Such behavior was found in the ternary systems H_2O – K_2SO_4 – $KLiSO_4$ and H_2O – SiO_2 – $Na_2Si_2O_5$ [1].

Ternary class 1-2-1. Solubility behavior in ternary class **1-2-1** is characterized by the increasing of solubility of type **2** salt with increasing a concentration of the second salt (type **1** salt) and by the change of sign of temperature coefficient of salt solubility (t.c.s.) from negative to positive in ternary solutions. Such phase behavior was observed in the system NaCl – Na_2SO_4 – H_2O, KCl – K_2SO_4 – H_2O, K_2CO_3 – Na_2CO_3 – H_2O, Na_2HPO_4 – Na_3PO_4 – H_2O etc. [1, 10], where NaCl, KCl, K_2CO_3, Na_2HPO_4 belong to type **1** salt and aqueous systems with Na_2SO_4, K_2SO_4, Na_2CO_3, Na_3PO_4 are the binary systems of type **2d'**. The metastable immiscibility region, spreading from the binary subsystem of type **2d'**, usually does not transform into stable equilibria. Nevertheless, the tie-line form of solubility isotherms at subcritical temperatures shows that the metastable immiscibility region takes place very

close to the stable solubility surface. A transition of the metastable immiscibility region into stable equilibria through the immiscibility of solid saturated solutions at vapor pressure was established in the system $Na_2HPO_4 - Na_3PO_4 - H_2O$ [10], where both water-salt subsystems have the immiscibility regions of type **d** that is stable in the $Na_2HPO_4 - H_2O$ system (type **1d**) and metastable in the $Na_3PO_4 - H_2O$ system (type **2d'**). The topological scheme **IIIβ-3** (Fig. 2) shows a construction of complete phase diagram for such ternary systems as $Na_2HPO_4 - Na_3PO_4 - H_2O$.
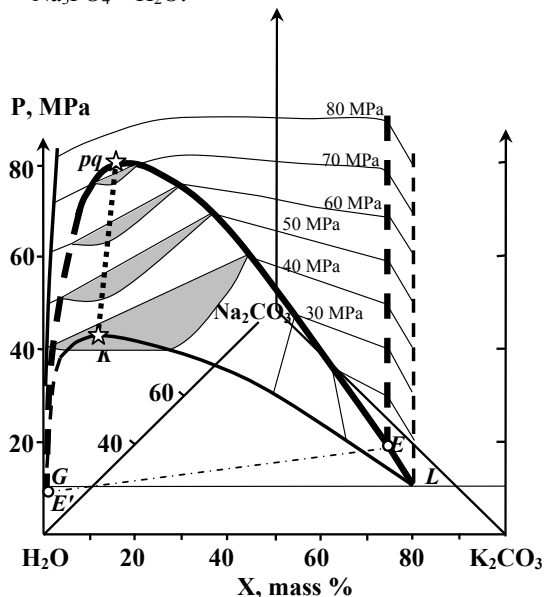
Fig.3 Three-dimensional P-X diagram of the ternary system $Na_2CO_3 - K_2CO_3 - H_2O$ at 425 ^{o}C.

Stars are the critical points in binary (point **K** (L=G)) and ternary (point **pq** ($L_1=L_2$-S_{Na2CO3})) systems; points **L** and **G** are the compositions of liquid and gas solutions equilibrium with solid K_2CO_3 in the binary system $K_2CO_3 - H_2O$; points **E** and **E'** (open circles) are the compositions of liquid and gas solutions, respectively, in equilibrium with two solid solutions in the ternary system; dotted line **K-pq** is a critical curve in ternary system; heavy lines are the compositions of ternary solutions in three-phase equilibria; solid lines are the compositions of binary solutions in two-phase equilibria; dashed lines show the extrapolated parts of heavy and solid lines; thin lines show a composition of ternary solutions in two-phase equilibrium (L-G, L_1-L_2, Fl-S) at constant pressure; shaded parts show the isobaric cross-sections of two-phase regions L-G and L_1-L_2.

In the case when the metastable three-phase immiscibility region of type **d** spreading from the

binary subsystem of type **2d'** does not transform into stable equilibria, a homogeneous supercritical fluid region is bounded by the continuous monovariant critical curve pQ (see Item 5). The T-X* schemes **IVα-2** in Fig. 2 show such behavior in a vicinity of binary subsystem A-C of type **2d'**. Ternary critical curve pQ starts in the binary critical endpoint "p" as a critical endpoint locus of the nature L=G-S and transforms continuously into the equilibrium $L_1=L_2$-S with increasing of pressure (and temperature) on the way to the binary critical endpoint Q ($L_1=L_2$-S).

The first experimental data on a behavior of the critical curve pQ in a ternary system of class **1a-2d'-1a** with metastable three-phase immiscibility region were obtained recently for the system $Na_2CO_3 - K_2CO_3 - H_2O$.

Figure 3 shows the three-dimensional P-X diagram of the ternary system at constant temperature (425 ^{o}C) where one can see how the homogeneous supercritical fluid saturated with solid Na_2CO_3 breaks down into two solutions upon addition of K_2CO_3 to the aqueous Na_2CO_3. Phase separation of solid saturated supercritical fluid originates from the critical point **pq** ($L_1=L_2$-S_{Na2CO3}) that belongs to the ternary critical curve pQ. Monovariant phase equilibria $L_1=L_2$ and L_1-L_2-S_{Na2CO3} originated in this critical point transform continuously into the equilibria L=G and L-G-S_{Na2CO3} with decreasing of pressure.

References

[1] V. M. Valyashko, *Phase Equilibria and Properties of Hydrothermal Systems (Russ.)*, Nauka, Moscow (1990).
[2] V. M. Valyashko, *Phys. Chem. Chem. Phys.*, **4,** 1178 (2002).
[3] R. L. Scott and P. N. Van Konynenburg, *Faraday Discuss. Chem. Soc.*, **49,** 87 (1970).
[4] L. Z. Boshkov, *Dokl. Akad. Nauk SSSR*, **294**, 901 (1987).
[5] V. M. Valyashko, *Pure & Appl. Chem.*, **74,** 1871 (2002).
[6] C. J. Peters and K. Gauter, *Chem. Rev.*, **99,** 419 (1999).
[7] V.M. Valyashko, B.R.Churagulov, *The Experimental Determination of Solubilities.Ch.4.3,* Edts. G.T.Hefter, R.P.Tmkins, Wiley&Sons (2003)
[8] M. A. Urusova and V. M. Valyashko V. M., *Russ. J. Inorg. Chem.*, **43**, 948 (1998).
[9] V. M. Valyashko and M. A. Urusova, *Russ. J. Inorg. Chem.*, **41,** 1297 (1996).
[10] M. A. Urusova and V. M. Valyashko, *Russ. J. Inorg. Chem.*, **46,** 777 (2001).