DERIVATION OF FLUID AND COMPLETE PHASE DIAGRAMS FOR TERNARY SYSTEMS WITH ONE VOLATILE COMPONENT AND IMMISCIBILITY PHENOMENA IN TWO BINARY SUBSYSTEMS

V.M. Valyashko

Kurnakov Institute of General and Inorganic Chemistry RAS,
Leninsky str. 31, 119991, Moscow, RUSSIA
E-mail: Valyashko@IGIC.RAS.RU & Fax: 7 (095) 954-1279

Four main types of binary fluid phase diagrams and available experimental data on binary systems were used as a starting point for derivation of the systematic classification of binary complete phase diagrams by the method of continuous topological transformations. This method and the 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. The results gained from the analysis of derived fluid and complete phase diagrams of ternary systems are represented.

INTRODUCTION

The theoretical derivation of phase diagrams, developed by van der Waals and his school at the end of XIX - beginning of XX century [1], was made by a topological method after the main features of a geometry of thermodynamic surfaces (van der Waals surfaces) were obtained from limited calculations (available at that time) using the equation of state. Since the first publication of Scott and van Konynenburg in 1970 on global phase behavior of binary fluid mixtures [2] the classical approach to the derivation of phase diagrams from the equations of state has changed from the topological method to the analytical method. However, such calculations do not permit study of phase equilibria with solid phases because a general liquid-gas-solid equation of state is absent.

The main objectives of this presentation are to demonstrate that the topological method on the level of schemes of phase diagrams (not on the level of thermodynamic surfaces as it was in the method of van der Waal's school) can be used for derivation of the complete phase diagrams, which describe not only fluid equilibria but also all the equilibria with solid phase in a wide range of temperature and pressures, and to show some results of such derivation.

The method of continuous topological transformation [3] is based on the premise that each type (or topological scheme) of phase diagram can be continuously transformed into another type 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 investigations of various equations of state and the boundary versions for such fluid mixtures can be borrowed from the global phase diagrams. Modifications of stable fluid phase equilibria in presence of a solid phase do not change the type and topological scheme of fluid phase 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, the parts of immiscibility regions and/or critical curves) is suppressed by solidification of the nonvolatile component and transforms into the metastable equilibria.

CLASSIFICATION OF BINARY COMPLETE PHASE DIAGRAMS

Scott and Konynenburg [2] classified six types (types I-VI) of binary fluid phase behavior, the type VII was added later by Boshkov [4]. However, this traditional classification includes only four main types of binary phase diagram (I, V, V and VII) with different combinations of fluid phase equilibria. Three other types (II, III and IV) are repeated these combinations and show the result of solid phase interference in fluid equilibria of types V, VI and VII. Therefore only the mentioned four types were used as the main types of fluid phase behavior in our classification (Figure 1) where they form four horizontal rows of the diagrams, designated as rows **a** (type I), **b** (type VI), **c** (type VII) and **d** (type V).

The systematic classification of complete phase diagrams (P-T projections) for binary systems, shown in Figure 1, was derived using the method of continuous topological transformation [3], consists of four horizontal rows (**a, b, c, d**) and three vertical columns (**1**, **1'**(**1''**), **2**) and is complete within the framework of the definite limitations [5].

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 in 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 fluid - solid" equilibria are absent in the diagrams from central column, but they appear in the diagrams of type **2** from the right column.

Diagrams from Figure 1 included in boxes and separated of neighboring complete phase diagrams are the boundary versions of binary phase diagrams. They contain the special points representing nonvariant equilibria in ternary systems and demonstrate continuity of topological transformation of one binary type of a complete phase diagram into another.

DERIVATION OF FLUID AND COMPLETE TERNARY PHASE DIAGRAMS

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

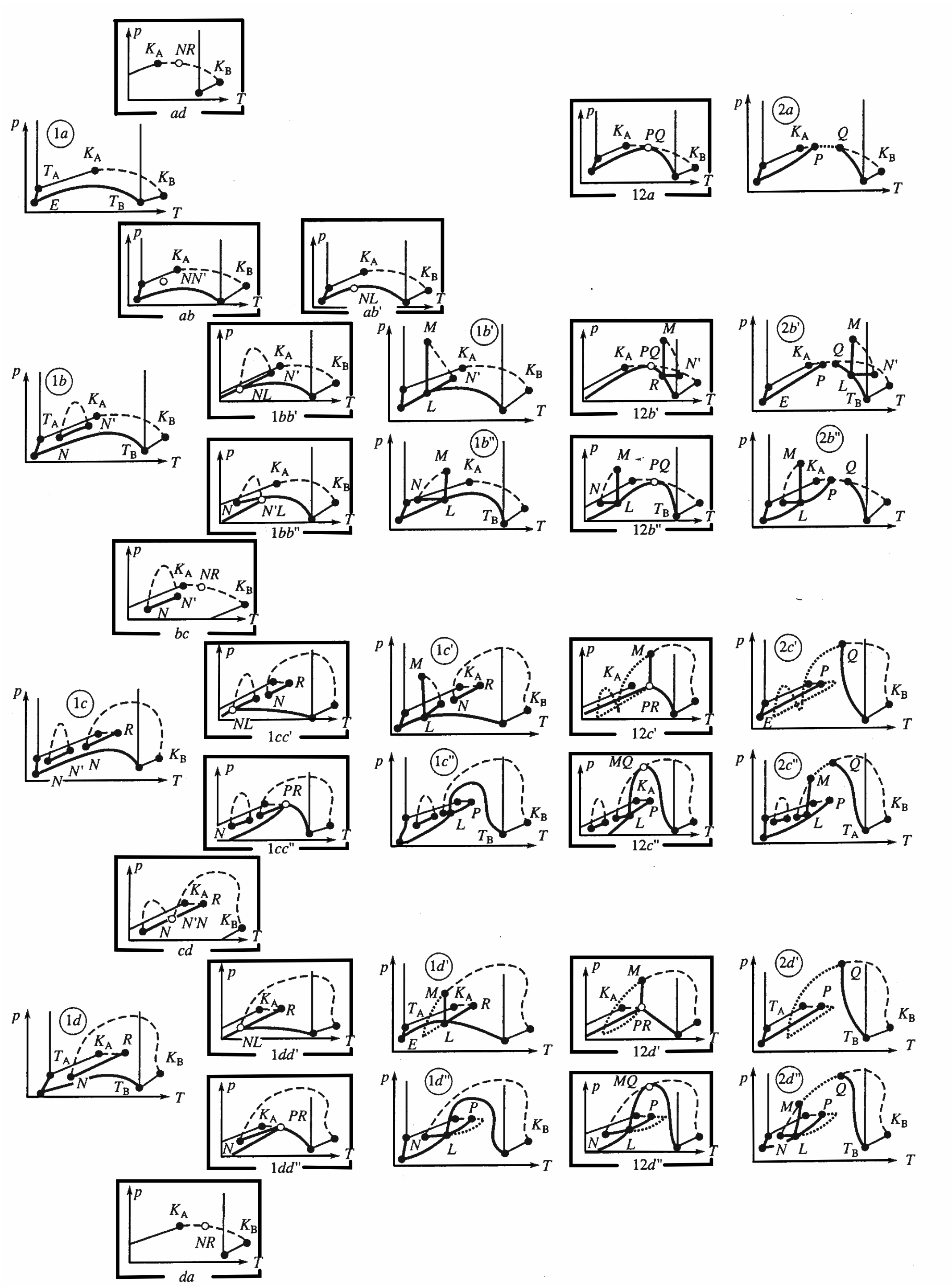

Figure 1: Systematic classification of binary complete phase diagrams (***p*-*T*** projections).

The diagrams shown in frames are the boundary versions. 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.

process may be imagined as a continuous phase diagram transformation of quasi-binary sections of the ternary system with a constant volatile component (water in the case of water-salt systems) and a continuously changing non-volatile component (salt component in the case of water-salt systems) from one non-volatile component to another. This constitutes so-called "quasi-binary approach" to the ternary phase equilibria.

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 on the same figure as a set of complete phase diagrams corresponding to the quasi-binary sections. Such sets include the boundary versions of phase diagrams, which show ternary nonvariant points that should appear in the studied three-component systems [5].

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 [5, 6]. 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**) [5].

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. A continuous topological transformation of one topological type of ternary fluid phase diagram into another in the frame of one ternary class was carried out by merging together the ternary nonvariant points and by tangency of one monovariant curve to another in accordance with the rules formulated in [5]. The result of derivation is 39 schemes of ternary fluid phase diagrams.

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 solid continuous 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

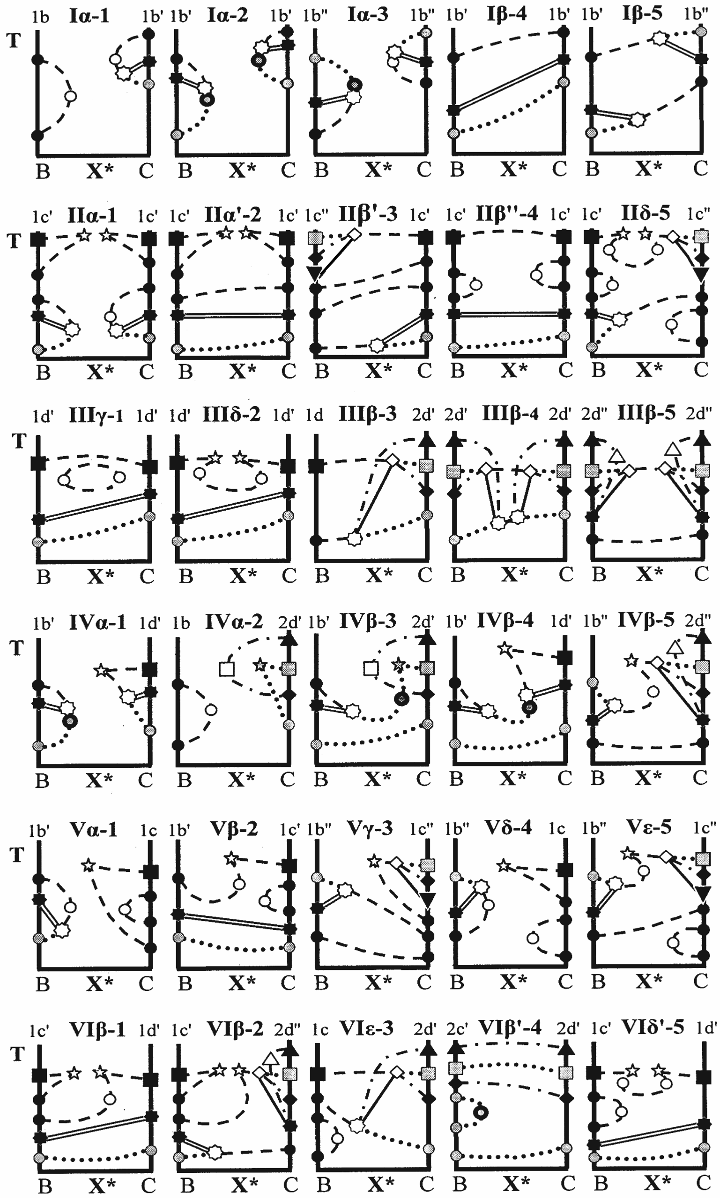

Figure 2: ***T-X**** projections (schemes) of some complete phase diagrams for ternary systems with one volatile component (A) and immiscibility phenomena in two binary subsystems (A-B, A-C).

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) phase equilibria in binary and ternary systems*:**

- ▲ - Q ((L_1=L_2-S)
- ■ - R (L_1=G-L_2)
- ● - N (L_1=L_2-G)
- ◆ - P (L=G-S)
- ▼ - L (L_1-L_2-G-S)
- ✹ - L (L_1-L_2-G-S) + M (L_1=L_2-S)
- ▢ - R **m/s** (L_1=G-L_2)
- ○ - N **m/s** (L_1=L_2-G)
- ◉ - N'N **m/s** (L_1=L_2-G)
- ☆ - NR **m/s** (L_1=G=L_2)
- ☆ - NR (L_1=L_2=G)
- □ - PQ (L=G-S)
- ○ - N'N (L_1=L_2-G)
- ✩ - NL (L_1=L_2-G-S)
- ◇ - PR (L_1=G-L_2-S)
- △ - MQ (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)

(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** [7]. 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 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.

ACKNOWLEDGEMENTS

This work was supported by the Russian Fondues of Basic Research under Grant no. 01-03-32770 and by the INTAS Project No. 00-640.

REFERENCES:

[1] VAN DER WAALS, J.D. and KOHNSTAMM, P., Lehrbuch der Thermodynamik, Barth, Leipzig, **1912**

[2] SCOTT, R.L. and VAN KONYNENBURG, P.N., Faraday Discuss. Chem. Soc., Vol. 49, **1970**, p.87

[3] VALYASHKO, V.M., Phase equilibria and Properties of Hydrothermal Systems (Russ.), Nauka, Moscow, **1990**

[4] BOSHKOV, L.Z., Dikl. Akad. Nauk SSSR, Vol. 294, **1987**, p.901

[5] VALYASHKO, V.M., Phys. Chem. Chem. Phys., Vol. 4, **2002**, p.1178

[6] VALYASHKO, V.M., Pure & Appl. Chem., Vol. 74, **2002**, p.1871

[7] PETERS, C.J. and GAUTER, K., Chem. Rev., Vol. 99, **1999**, p.419