Bifurcation and “self-organization” of a system

M Aldabergenov\(^1\), G Balakaeva\(^2\)

\(^1\)Al-Farabi Kazakh National University, Almaty, Kazakhstan
\(^2\)K.I.Satpaev Kazakh National Technical University, Almaty, Kazakhstan

E-mail: aldabergenov_m@mail.ru

Abstract. Triangulation of a multicomponent system was shown on example of the CaO-SiO\(_2\)-H\(_2\)O system. "The Gibbs function normalized to the total number of electrons" was applied in order to reflect all the possible transformations of components of the system at non-equilibrium as well as at equilibrium conditions. The bifurcation points of the system are located at the each intersection of the line connected compositions of the interacting components and the stable secant line. It was shown the possibility of the "self-organization" processes which is based on the exchange as well as that reactions.

Introduction

Natural and technological objects are represented by multicomponent systems. Chemical and physico-chemical interactions of these systems are defined by the substance microstates. Geometric images of the multicomponent systems can be represented by the phase diagram which is based on the continuity and consistency principles [1] which reflects the transformation processes between components of a system. The “structure-property” diagram is the precise geometric model of the complex functions which are establishing the relationship between temperature, volume, concentration and the other physical and chemical factors which are determining the state of the open system. In other words, the “structure-property” diagram merges together chemical transformations of matter and space geometric transformations into one whole. The phase diagram allows to define phase boundaries of the different phases existing in the system as well as to reveal not pronounced chemical processes. Additionally it allows to high light the weak interparticle interactions that do not lead to the formation of new compounds or to the decomposition of existing phases [2]. The phase diagrams enables widely consider problems of physical chemistry and chemical thermodynamics, reflecting modern ideas about the properties of individual substances as well as their mixtures, phase and chemical equilibria, and surface phenomena jointly. They are widely used in search of new intermetallic compounds [3-5], the glass-forming systems in the crystalline, glassy and molten states [6-8], solid solutions [9,10], predicting of the properties of metastable states [11-13] , analysis of phase transitions and critical phenomena [14,15], the fabrication of composite materials [16,17], the processes of separation and purification of substances [18,19], the development of algorithms for constructing phase diagrams [20-21], and others [22-25] presently.

Study of the phase diagrams implies partitioning of the multidimensional figures on individual cells - media of the invariant points which are called triangulation. The topological [1,2], geometric [26,27] and thermodynamic [28,29] triangulation techniques are available at this moment. The main feature of the systems triangulation is the determination of the constituents forming only eutectic composition (single phase units). The constituents of a single phase unit do not form new compounds and do not
mutually interact, but those of different phase units interact with each other. Therefore the system triangulation gives possibility to determine the phase transitions occurring during, for example, exchange reactions, reactions of hydration and dehydration, reactions of polycondensation, conversion and complex formation. It allows predicting all the way of bifurcation of components and predict the existence of new compounds additionally.

The triangulation of the multicomponent open CaO-SiO$_2$-H$_2$O system was applied, as a collection of equilibrium and nonequilibrium states of the system components. A method of determination of the bifurcation points and "self-organization" of systems is developing in the present paper.

1. Method, results and discussion

Triangulation of the CaO-SiO$_2$-H$_2$O system (see Fig.1) is based on the Kurnakov theory [1] using the "the Gibbs function normalized to the total number of electrons" [30]. In the CaO-SiO$_2$-H$_2$O system the formation of 86 compounds was considered (Table I). The corresponding thermodynamic parameters were calculated using the ion increments method by Aldabergenov’s increments [30]. Our calculations show good consistency with the reference data presented by Glushko VP [31], the relative error does not exceed 0.9%. The Gibbs free energy of formation of many compounds presented in Table I were calculated for the first time.

A new concept of "The Gibbs function normalized to the total number of electrons" ($\Delta G_{298}^{\circ}$) [32] was proposed. Its physical meaning consists in determination of the chemical bonding as a collective effect of the electron-nuclear interaction. It is calculated by dividing of the Gibbs free energy of formation value of the compound to the total number of electrons in this compounds. In other words this function determines the density of the formation energy of the compound per electron. "The Gibbs function normalized to the total number of electrons" appropriately responds on the all changes occurring in the crystal structure of a compound. Additionally the function allows to assess compounds’ reactivity and stability [32]. It also can determine the value of the chemical potential and affinity, calculate entropy’s production and flow, calculate: - thermodynamic force and flux, - thermodynamic "probability" of interaction, - degree of conversion of components in a chemical reaction. Finally using the “The normalized Gibbs function” allows to perform the triangulation of multicomponent systems and establish the reaction mechanisms.

The triangulation is performed by partitioning of the large basic triangle into several small “subtriangles”, which are named by Kurnakov as simplex [1]. In Ref. [28] A.S.Trunin calls single phase unit (SPU). SPU’s are characterized by the formation of eutectic composition. Compounds belonged to one single SPU do not interact with each other, however those belonged to different SPU engage in interaction. In similar way it is possible to consider any interaction between components of the system.

Let us consider the interaction between Ca$_2$SiO$_4$.4H$_2$O (compound #42) and Ca$_3$Si$_2$O$_6$.4(OH)$_2$.2H$_2$O (compound #48) (see Table 1) in the exchange reactions. For this we draw a straight line 42-48 connecting the corresponding compositions, which intersects the following stability secants: 18-69; 39-69; 39-78; 38-78; 78-17; 78-37; 78-79; 69-79; 69-17; 69-82 (Fig. 1). The points of the intersections are called Radishchev’s points of conversion [33]. At these points the system becomes unstable and new solutions of evolution appear due to bifurcations. Therefore these points are also named as bifurcation points. The line 42-48 indicate that in the presence of a small displacement of the initial components of the system is abruptly switching between the stable states. These points can be named as symmetric bifurcations [34].

At Radishchev’s points [33] of conversion (or bifurcation points) the following reaction occur (we present only two reactions). The corresponding numbers are presented in Fig.1 for convenience.
Figure 1. Triangulation system CaO-SiO$_2$-H$_2$O

(Compounds #48 and #53 have identical compositions. Similar coincides are existing for other compounds #66 and #67; #59 and #73; #49 and #75; #65 and #81; #35 and #71; #83; #41 and #84; v8 and #9, #10, #11, #12, #13; #21 and #22; #24 and #25; #26 and #27, #28, #29, #30. Therefore only one number is shown for the coincided compounds)

Table 1. The values of the Gibbs free energy of formation ($-\Delta G_{298}^\circ$) and "The Gibbs function normalized to the total number of electrons" ($-\overline{\Delta G}_{298}^\circ$) of the compounds existing in the CaO-SiO$_2$-H$_2$O system

| Compounds       | $-\Delta G_{298}$, kJ/mol | % av. | $-\overline{\Delta G}_{298}^\circ$, kJ/mol.el |
|-----------------|----------------------------|-------|-----------------------------------------------|
|                 | 1                          | 2     | 3     | 4     | 5                                      |
|                 | by increments              | [31]  |       |       |                                        |
| 1. CaO          |                            | 603.5 | 21.55 |      |                                        |
| 2. SiO$_2$      |                            | 892.6 | 29.75 |      |                                        |
| 3. H$_2$O       |                            | 237.2 | 23.72 |      |                                        |
| 4. H$_2$Si$_4$O$_{29}$ | 12437.23                |       | 28.92 |      |                                        |
| 5. H$_2$Si$_8$O$_{17}$ | 7274.17                 |       | 29.10 |      |                                        |
| 6. H$_2$Si$_5$O$_4$ | 2111.11                  |       | 30.16 |      |                                        |
| 7. H$_2$Si$_6$O$_{17}$ | 7113.49                  |       | 30.93 |      |                                        |
| 8. H$_2$SiO$_3$ | 1250.60             |       | 31.26 |      |                                        |
| 9. H$_2$Si$_2$O$_6$ | 2501.19                 |       | 31.26 |      |                                        |
| 10. H$_2$Si$_4$O$_9$ | 3751.79                 |       | 31.26 |      |                                        |
| 11. H$_2$Si$_6$O$_{12}$ | 5002.38                 |       | 31.26 |      |                                        |
|   | 1          | 2            | 3       | 4       | 5       |
|---|------------|--------------|---------|---------|---------|
| 12 | H$_2$Si$_2$O$_5$ | 6252.98      | 31.26   |         |         |
| 13 | H$_2$Si$_4$O$_8$ | 7503.58      | 31.26   |         |         |
| 14 | H$_4$Si$_2$O$_9$ | 5392.47      | 31.72   |         |         |
| 15 | H$_4$Si$_2$O$_{10}$ | 4141.87    | 31.86   |         |         |
| 16 | H$_4$Si$_2$O$_7$ | 2891.28      | 32.13   |         |         |
| 17 | H$_4$Si$_4$O$_4$ | 1640.68      | 32.81   |         |         |
| 18 | H$_6$Si$_4$O$_6$ | 2099.28      | 29.99   |         |         |
| 19 | Ca(OH)$_2$   | 897.5        | 23.62   |         |         |
| 20 | Ca$_3$SiO$_3$ | 2788.84      | 2785.1  | 0.13    | 24.46   |
| 21 | Ca$_2$SiO$_4$ | 2185.34      | 2191.3  | 0.27    | 25.41   |
| 22 | Ca$_3$Si$_2$O$_{12}$ | 6460.24 |         |         | 25.04   |
| 23 | Ca$_4$Si$_3$O$_{18}$ | 9548.14 |         |         | 25.53   |
| 24 | Ca$_3$Si$_3$O$_7$ | 3724.29      | 3756.7  | 0.87    | 25.86   |
| 25 | Ca$_5$Si$_4$O$_{14}$ | 7362.80 |         |         | 25.57   |
| 26 | Ca$_5$SiO$_5$   | 1538.95      | 1543.9  | 0.32    | 26.53   |
| 27 | Ca$_2$Si$_2$O$_6$ | 3077.90      |         |         | 26.53   |
| 28 | Ca$_2$Si$_3$O$_9$ | 4616.85      |         |         | 26.53   |
| 29 | Ca$_4$Si$_6$O$_{18}$ | 9233.70 |         |         | 26.53   |
| 30 | Ca$_4$Si$_2$O$_{21}$ | 10772.65 |         |         | 26.53   |
| 31 | Ca$_4$Si$_2$O$_{17}$ | 8587.31 |         |         | 26.84   |
| 32 | Ca$_4$Si$_2$O$_{17}$ | 5509.41 |         |         | 27.01   |
| 33 | Ca$_4$Si$_2$O$_{23}$ | 2431.51 |         |         | 27.63   |
| 34 | Ca$_4$Si$_2$O$_{19}$ | 3324.07 |         |         | 28.17   |
| 35 | Ca$_4$Si$_2$O$_{3}$,16H$_2$O | 1574.15 |         |         | 26.41   |
| 36 | Ca$_4$Si$_2$O$_{3}$,H$_2$O | 1758.95 |         |         | 25.87   |
| 37 | Ca$_4$Si$_2$O$_{3}$,H$_2$O | 1978.95 |         |         | 25.37   |
| 38 | Ca$_4$Si$_2$O$_{2}$,5H$_2$O | 2088.95 |         |         | 25.17   |
| 39 | Ca$_4$Si$_2$O$_{3}$,3H$_2$O | 2198.95 |         |         | 24.99   |
| 40 | Ca$_4$Si$_2$O$_{3}$,2H$_2$O | 2405.34 |         |         | 25.06   |
| 41 | Ca$_4$Si$_2$O$_{4}$,1,7H$_2$O | 2442.74 |         |         | 25.00   |
| 42 | Ca$_4$Si$_2$O$_{4}$,4H$_2$O | 3065.34 |         |         | 24.33   |
| 43 | Ca$_4$Si$_2$O$_{4}$,3H$_2$O | 2651.51 |         |         | 27.06   |
| 44 | Ca$_4$Si$_2$O$_{4}$,2H$_2$O | 2871.51 |         |         | 26.59   |
| 45 | Ca$_4$Si$_2$O$_{4}$,3H$_2$O | 3091.51 |         |         | 26.20   |
| 46 | Ca$_5$Si$_2$O$_{6}$,(OH)$_2$ | 3553.37 |         |         | 27.76   |
| 47 | Ca$_2$Si$_2$O$_{6}$,H$_2$O | 3297.90 |         |         | 26.17   |
| 48 | Ca$_2$Si$_2$O$_{5}$,(OH)$_2$,2H$_2$O | 4393.59 |         |         | 25.25   |
| 49 | Ca$_2$Si$_2$O$_{5}$,2H$_2$O | 4367.57 |         |         | 26.31   |
| 50 | Ca$_2$Si$_2$O$_{5}$,2,5H$_2$O | 4477.57 |         |         | 26.18   |
| 51 | Ca$_2$Si$_2$O$_{5}$,1,5H$_2$O | 6085.58 |         |         | 27.54   |
| 52 | Ca$_3$Si$_2$O$_{2}$,H$_2$O | 3944.29 |         |         | 25.61   |
| 53 | Ca$_3$Si$_2$O$_{2}$,3H$_2$O | 4384.29 |         |         | 25.20   |
| 54 | Ca$_3$Si$_2$O$_{2}$,H$_2$O | 4836.85 |         |         | 26.29   |
| 55 | Ca$_3$Si$_2$O$_{2}$,7H$_2$O | 8834.53 |         |         | 26.45   |
| 56 | Ca$_3$Si$_2$O$_{13}$,(OH)$_4$ | 7753.13 |         |         | 27.30   |
| 57 | 3Ca$_3$Si$_2$O$_{13}$,(OH)$_4$,4H$_2$O | 24139.39 |         |         | 27.06   |
| 58 | Ca$_4$Si$_2$O$_{10}$,H$_2$O | 5473.24 |         |         | 25.82   |
| 59 | Ca$_4$Si$_2$O$_{10}$,1,5H$_2$O | 5583.24 |         |         | 25.73   |
Let us consider the dehydration process of the Ca$_2$SiO$_4$(OH)$_2$.2H$_2$O compound.

The dehydration process obeys the following postulates [36]:

1. The water removal takes place only along the phase equilibria line which is connecting the compound with the water corner (see Fig. 1);
2. If the compound under going dehydration is not directly related to the pole of water, then at the reaction of conversion occurs or bifurcation take place for compounds related to the pole of this compound.

The first reaction occurs with a large gain in energy.

Let us consider the dehydration process of the Ca$_2$SiO$_4$(OH)$_2$.2H$_2$O compound (see #48 in Fig. 1). The dehydration process obeys the following postulates [36]:

1. The water removal takes place only along the phase equilibria line which is connecting the compound with the water corner (see Fig.1);
2. If the compound under going dehydration is not directly related to the pole of water, then at the reaction of conversion occurs or bifurcation take place for compounds related to the pole of this compound.

Each chemical reaction is characterized by affinity (A), which can be found using the theory of de Donder [35]: A = 4.53 kJ / mol.el.
The Ca$_3$Si$_2$O$_6$(OH)$_2$.2H$_2$O compound (#48) is not directly connected with the water corner and it is not affected by the conversion reaction then. However, in accordance with a second postulate, the dehydration process begins from the decomposition (bifurcation) of Ca$_3$Si$_2$O$_6$(OH)$_2$.2H$_2$O to compounds #41, #69, #17 and #82 which are located on the stability diagonals connected with the corner of the parent silicate. Additionally so-called asymmetric bifurcation also occurs, which is associated with the conversion of the original salt into the four following compounds of the system:

$$48 = 41 + 69 + 17 + 82:$$

$$126[Ca_3Si_2O_6(OH)_2.2H_2O] = 100[Ca_2SiO_4.1.17H_2O] + 13[Ca_6Si_2O_7(OH)_6] + 6H_4SiO_4 + 10[Ca_{10}Si_2O_{18}(OH)_6.18H_2O] \quad (3)$$

$$\Delta rG^o = 354.09 \text{ kJ (2.81 kJ/mol per original salt). A} = 82.35 \text{ kJ/mol.el.}$$

In this reaction H$_4$SiO$_4$ is connected with the water corner only and subjected to the dehydration process with the water elimination by the reaction (4) and (5):

$$17 = 18 + 16:$$

$$5H_4SiO_4 = H_8SiO_6 + 2H_2Si_2O_7 \quad (4)$$

$$\Delta rG^o = 321.56 \text{ kJ (64.31 kJ/mol on the initial salt). A} = 29.31 \text{ kJ/mol.el.}$$

The evolvement of water from H$_4$SiO$_4$ occurs only by the conversion reaction:

$$18 = 3 + 17:$$

$$H_8SiO_6 = 2H_2O + H_4SiO_4 \quad (5)$$

$$\Delta rG^o = -15.8 \text{ kJ/mol on the initial salt. A} = 26.54 \text{ kJ/mol.el.}$$

The conversion reaction may be continue until silica is produced:

$$16 = 17 + 15:$$

$$2H_2Si_2O_7 = H_3SiO_4 + H_2Si_5O_{10} \quad (6)$$

$$\Delta rG^o = 0 \text{ kJ/mol on the initial salt. A} = 32.54 \text{ kJ/mol.el.}$$

$$15 = 16 + 14:$$

$$2H_2Si_5O_{10} = H_6Si_3O_7 + H_{10}Si_4O_{13} \quad (7)$$

$$\Delta rG^o = 0 \text{ kJ/mol on the initial salt. A} = 32.54 \text{ kJ/mol.el.} \text{ rG}^o = 0 \text{ kJ/mol on the initial salt. A} = 31.99 \text{ kJ/mol el. and so on until Si}_2O_2 \text{ is produced.}$$

As it is shown in (6) and (7), the reactions are characterized by high degree of affinity and the conversion process does not actually require for external influence. The conversion reactions along the SiO$_2$-H$_2$O (2-3) line leads to the formation of various silicic acids and SiO$_2$.

The compounds formed by the reaction (3), also undergo the bifurcation transformations further in accordance with the second postulate, for example:

$$69 = 20 + 19 + 42 + 18 + 39 + 78 + 79 + 17 + 82 + 48 + 41:$$

$$143[Ca_6Si_2O_7(OH)_6] = 137Ca_3SiO_5 + 211Ca(OH)_2 + 2[Ca_5SiO_4.4H_2O] + H_4SiO_4 + CaSiO_3.3H_2O + [Ca_9Si_2O_7HSi_2O_3(OH)_6.6H_2O] + [Ca_6Si_6O_{18}(OH)_6.6H_2O] + 20H_2SiO_4 + [Ca_{10}Si_2O_{18}(OH)_6.18H_2O] + 100[Ca_2SiO_4.1.17H_2O] + [Ca_3Si_2O_6(OH)_2.2H_2O] \quad (8)$$

$$\Delta rG^o = 0 \text{ kJ/mol on the initial salt. A} = 32.54 \text{ kJ/mol.el.} \text{ rG}^o = -21450.37 \text{ kJ (-143.0 kJ/mol to original salt). A} = 261.56 \text{ kJ/mol.el.}$$
In this reaction the products $\text{H}_2\text{SiO}_4$ and $\text{Ca(OH)}_2$ are connected with the water corner. The dehydration process of $\text{H}_2\text{SiO}_4$ proceeds by reactions (4) and (5). The dehydration process of $\text{Ca(OH)}_2$ proceeds according to the following conversion mechanism with the formation of water and calcium oxide:

$$19 = 1 + 3: \quad \text{Ca(OH)}_2 = \text{CaO} + \text{H}_2\text{O} \quad (9)$$

$$\Delta rG^o = 56.8 \text{ kJ/mol on initial salt. } A = 21.65 \text{ kJ/mol.el.}$$

Analysis of the dehydration reaction of $\text{Ca}_9\text{Si}_2\text{O}_{31}(\text{OH})_6.18\text{H}_2\text{O}$ (#82), $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6.6\text{H}_2\text{O}$ (#79), $\text{Ca}_9\text{Si}_3\text{O}_{10}\text{HSi}_2\text{O}_3\text{H(OH)}_9.6\text{H}_2\text{O}$ (#78), $\text{Ca}_2\text{SiO}_4.1.17\text{H}_2\text{O}$ (#41) and $\text{CaSiO}_3.3\text{H}_2\text{O}$ (#39) continue in accordance with the second postulate.

After wards the dehydration processes of $\text{Ca}_9\text{Si}_2\text{O}_{31}(\text{OH})_6.18\text{H}_2\text{O}$ (#82), $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6.6\text{H}_2\text{O}$ (#79), $\text{Ca}_9\text{Si}_3\text{O}_{10}\text{HSi}_2\text{O}_3\text{H(OH)}_9.6\text{H}_2\text{O}$ (#78), $\text{Ca}_2\text{SiO}_4.1.17\text{H}_2\text{O}$ (#41) and $\text{CaSiO}_3.3\text{H}_2\text{O}$ (#39) continue in accordance with the second postulate.

The dehydration reaction occurring in the $\text{CaO-SiO}_2$-$\text{H}_2\text{O}$ system showed a possibility to become the natural structure as well as to reach the equilibrium state through "self-organization". It was established that "self-organization" occurs in the result of the exchange and conversion reactions.

Conclusions

The singular triangulation is a rational splitting of the primary simplex (triangle) on secondary triangles using singular secants. It helps to determine direction of reactions, to establish the nature and character of the individual phases in any part of systems and make conclusions about the character of the system under investigation. The most easiest way of triangulation can be carried out using so called "The Gibbs function normalized to the total number of electrons".

The dehydration reaction occurring in the $\text{CaO-SiO}_2$-$\text{H}_2\text{O}$ system showed a possibility to become the natural structure as well as to reach the equilibrium state through "self-organization". It was established that "self-organization" occurs in the result of the exchange and conversion reactions.

Reference

[1] Kurnakov N.S. Selected labors. Moscow: 1960 *Academy of Science of USSR*, 565
[2] Anosov V.J., Ozerov M.I., Fialkov U.Y. 1976 *Nauka* 504
[3] Chen M., Hallstedt B., Gauckler L.J. 2005 *Solid State Ionics* **176** 1457
[4] Lutsyk V.I., Vorobyova V.P. 2011 *Advanced Materials* **13**, 191
[5] Kosjakov V.I. 2008 *Journal of inorganic chemistry* **T.53**, 6 1020
[6] Pavlyuchkov D., Savinukh G., Fabrichnaya O. 2013 *Advanced Engineering Materials* **15**, N7, 618
[7] Lutsyk V.I. 2012 *Bulletin BSC SB RAS.* **1** (5) 78
Ushakov V.M., Borisova N.V. Vitrification and alkali silicate melts alkali borates / Materials XV Inter. Conf. on Chemical Thermodynamics in Russia. Moscow, 2005. - P.35.

Trahtenberg B.F., Kenis M.S., Krestyanov V.I., Troshina L.V. Diagnostics of the main mechanisms of technological heredity // Foundry. 1999. №1. p.13-15.

Kosjakov V.I., Shestakov V.A., Grachev E.V. Enumeration fusion diagrams of ternary systems with compounds of constant composition // Journal. Inorganic Chem. 2010. T.55. №4. P.662-670.

Nazmutdinov A.G., Nesterov T.N., Nesterov I.A., Vodenkova N.N. Investigation and prediction of properties of binary mixtures of organic substances / Materials XV Inter. Conf. on Chemical Thermodynamics in Russia. Moscow, 2005. - P.113.

Anisimov M.P., Fominih E.G., Akimov S.V., Trilis A.V. Elements of topology region of existence of metastable states of the two-component vapor // Journal. Fiz. chem. 2010, T.84, №3, P.427-433.

Ray A.K., Chalam M., Peters L.K. Homogeneous nucleation of binary vapours partially miscible in liquid state //J.Chem. Phys. 1986. V.85. №4. P.2161.

Aliiev A.M., Stepanov G.V. Effect of extractables on the critical parameters of supercritical fluids / Materials of XV Inter. Conf. on Chemical Thermodyn.in Russia. Moscow. 2005. - P.137.

Anisimov M.P., Hopke P.K. Nucleation Rate Surface Topologies far Binary Systems //J.Phys. Chem. B. 2001, 105. P. 11817-11822.

Wu P., Eriksson G., Pelton A.D. Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the CaO-FeO, CaO-MgO, CaO-MnO, FeO-MgO, FeO-MnO, and MgO-MnO Systems//J.Am.Caram. Soc. 1993, 76(8). P.2065-2075.

Aldabergenov M.K, Balakayeva G.T, Massimov K.K, Tusupbekov K.I. Composite borosilicate container for radioactive waste storage /Thesis.pres. VII All-Russian Scientific. Conf. "Ceramics and composite materials", Syktyvkar. - 2010.- P.7-8.

Lutsyk V. Phase diagram as a tool of metallurgist and materials scientist //proceedings of 46th International October Conf. on Mining and Metallurgy. Bor, Serbia, 2014. P. 148-151.

Klimova M.V. Trunin A.S. Modelling and identification of trees of four-phase reciprocal salt systems with different types of chemical interaction. Samara: Samara State Techn.Univ. 2005-120p.

Lutsyk V.I., Vorob'eva V.P. Computer models of eutectic type Txy diagrams with allotropy. Two inner liquidus fields of two low-temperature modifications of the same component // Journal of Thermal Analysis and Calorimetry. 2010. V. 101. No 1. P. 25-31.

Connell R.G. Tutorial on Flow Diagrams: A Tool for Developing the Structure of Multicomponent Phase Diagrams //J.Phase Equilibria and Diffusion. 1994. V.5. No 1.–P.6-19.

Cheynet B., Bonnet C., Stankov M. GEMINI-DiagPlot: 2D & 3D ternary phase diagrams. CALPHAD, 2009; 33:312-6.

Miura S. Geometrical approach to reaction schemes of multicomponent phase diagrams // J.Phase Equilib. Diffus. 2006. – P.34-36.

Chuvakov A.V., Truin A.S., Morgunova O.E. Theory and Methodology of differentiation of multicomponent systems. Samara: Samara State Techn.Univer. 2007.–117p.

Lutsyk V.I. Heterogeneous design: phase diagram - microstructure - materials genotype // Phase Diagrams in Materials Science. Stuttgart, Germany: Materials Science International Services, GmbH. 2004. - P.304-306.

Posypayko V.I. Methods of investigation of multicomponent systems.M.:Nauka,1978.- 255 p.

Truin A.S. A comprehensive research methodology of chemical interaction and heterogeneous equilibria in multicomponent salt systems // Journal of Applied Chem.-1983. T.28, V.1.- P.174-179.
[28] Aldabergenov M., Balakaeva G., Kokibasova G. Triangulation of the MgO-Al2O3-H2O system as applied to the hydration of magnesium aluminates and the dehydration of their hydrates //J. of Physical Chemistry. 2002, Vol.76, No. 5. P.791-795.
[29] Aldabergenov M.K, Balakayeva G.T Triangulation of multicomponent systems based on thermodynamic functions / "Actual problems of modern science", Proceedings of 3 Intern. forum, Samara, 2007. - Part 9., Issue 1. - P.39-43. http://ROSMAN.NET.RU.
[30] Aldabergenov M., Balakaeva G., Kassenov B. Applied Chemical Thermodynamics. Berlin :: LAP Lambert, 2012. - 350p.
[31] Glushko V.P. (Ed.), Thermal constants of compounds. Moscow, VINITI, 1970, Vol.4, 320p.
[32] Balakaeva G., Aldabergenov M. The Gibbs function normalized to the total number of electrons // Journal of Materials Science and Engineering B. 2 (6), 2012. P.394-403.
[33] Radishchev V.P. Multicomponent sistems.- M : ANSSSR, 1964.- T. I.- 540 p.
[34] Prigogine I., Kondepudi D. Modern Thermodynamics from heat engines to dissipative structures. Moscow: Mir, 2002. - 462p.
[35] De Donde T. L'Affinite. - Paris: Gauthiers-Villars, 1927.
[36] Aldabergenov M.K., Balakaeva G.T. Reactions of dehydration and polycondensation the system K2O-P2O5-H2O // Doklady NAS RK - 1994, №2.- P.54-58.
[37] Haken H. Information and self-organization. Moscow: Mir, 1991. - 240 p