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Phase Diagram Triangulation: Topology, Classification, Enumeration, Experiment Planning

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Abstract

The work is aimed at studying structural regularities of isobaric-isothermal subsolidus cross-sections of ternary phase diagrams with either stoichiometric phases or limited solid solutions. Topological cross-section scheme is presented in the form of a graph with trivalent inner faces. The graph contains not more than three bivalent vertexes. The work presents the relation between quantity parameters of the graphs. Their generation algorithm has been developed and carried out in the form of a program. The experiment planning program on the construction of cross-sections in real phase diagrams has been carried out.

1. Introduction

The space (*T*-*x*-*y*) of isobaric ternary phase diagram is a prism, with (*x*, *y*) composition simplex lying on the base, while the lateral edges are parallel to temperature axis *T*. Phase diagram is a complex three-dimensional structure in the form of space partition to the volumes corresponding to existence phases and phase complexes. Experimental investigation of isothermal cross-sections is one of the main methods to study isobaric *T*-*x*-*y* diagrams. Let the domain of existence of phases α, β and г present in such a cross-section. The domain of existence of ternary phase complex αβγ is a triangle, where the vertexes belong to the boundaries of one-phase domains and the laterals – to two-phase domains αβ, αγ and βγ. Each of them is formed from a continuous set of linear tie lines joining the composition points

of coexisting phases [1, 2]. Let's consider an isothermal cross-section which contains neither liquid nor gas phases. The exterior outline of the cross-section is a Gibbs triangle, with the vertexes corresponding to the components, i.e. having coordinates (0, 0), (0, 1) and (1, 0). Let's consider the case when there are no continuous solid solutions in the cross-section. Then one-phase, two-phase and three-phase domains may be substituted by points, lines and triangles correspondently. The points of binary compounds with coordinates (x, 0), (0, y), and (x, 1 – x) lie on the sides of the outline. The points of ternary compounds with coordinates (x, y) are situated inside the Gibbs triangle. In this case, straight line segments joining the compositions of coexisting phases divide this triangle into the set of intrinsic triangles which symbolize three-phase complexes. The obtained triangulation scheme reflects the topology of an isothermal subsolidus cross-section of a phase diagram. If in the cross-section of a real diagram there are only stoichiometric phases, the triangulation scheme coincides with the isothermal cross-section. Information on phase diagrams is necessary for the synthesis of new phases as well as obtaining one- and multiphase materials. Therefore, experimental studies of isothermal cross-sections are being carried out; the results of the research are placed in various data bases. In this connection, forecasting the possible triangulation schemes and their classification as well as optimization of the experiments on building isothermal cross-sections seems especially urgent.

Let q phases be present in the system and for each of them the dependence of Gibbs energy on composition $G_i(x_i, y_i)$ is known, where $1 \le i \le q$. As such, it is easy to calculate the value G for a random mixture of phases with total composition (x, y). Let's build the surface min $G(x, y)$ corresponding to the minimal value of G in any point of the Gibbs triangle (x, y). Isothermal cross-section T-x-y of the phase diagram represents the projection of this surface on the Gibbs triangle. Thus, if we measure thermodynamic properties of the phases, isothermal cross-section can be computed. With the shortage of thermodynamic data and the complexity of obtaining them, usually isothermal cross-sections are defined experimentally. For this purpose, the set of samples with different compositions are synthesized and brought into equilibrium state by long-duration annealing at a preset temperature. Then, the obtained phases and their compositions are identified in each particular sample.

When the data on thermodynamic properties of the phases in the system is lacking, it seems possible to construct a triangulation scheme for the system with the given binary and ternary compounds with the help of geometrical thermodynamics. To this end, random values G_i are assigned to each stoichiometric phase (x_i, y_i), after that a minimal surface $G(x, y)$ is built. Its projection on the Gibbs triangle represents a triangulation scheme. Varying G_i, one

can construct all possible triangulation schemes for a predetermined set of phases. This method is useful to visualize thermodynamic approach, but it seems rather useless for enumerating all possible triangulation variants, especially for the systems with a large number of compounds. To solve this task in general case, it is relevant to use the topological method which we applied for enumerating ternary solid-liquid diagrams [3]. The set of topological characteristics of the diagrams can be used for their classification [4]. It is necessary to mention that topological approach has also been applied to describe phase diagrams of both one-component and binary systems [5-7].

2. Topological properties of triangulation schemes

Let's consider subsolidus cross-section of the system with M binary and N ternary compounds. Its triangulation scheme is a graph with v vertexes, f faces and e edges. Let $v_{ex} = e_{ex} = M + 3$ vertexes and edges belong to the outer face of the graph (*component face*) which is situated on the outline of the Gibbs triangle. As $v_{in} = N$ of the vertexes and e_{in} of the edges being situated inside the outline. The graph has an multiangular outer face and $f - 1$ inner triangular faces. For such graphs, the ratios [8] are true

$$M + 3 + 3(f - 1) = 2e. \tag{1}$$

$$f = M + 2N + 2, \qquad e = 2M + 3N + 3, \qquad e_{in} = M + 3N, \qquad v = M + N + 3. \tag{2}$$

$$\sum(6 - m)v_m = 2(M + 6), \quad \sum(4 - m)v_m = 6 - 2N, \tag{3}$$

where v_m – the number of m-valent vertexes.

The example of triangulation in the system when $M = 4$, $N = 2$ is shown in Figure 1. For this diagram $f = 10$, $v = 9$, $v_{ex} = 7$, $e = 17$, $e_{in} = 10$, $e_2 = e_5 = e_6 = 1$, $e_3 = e_4 = 3$.

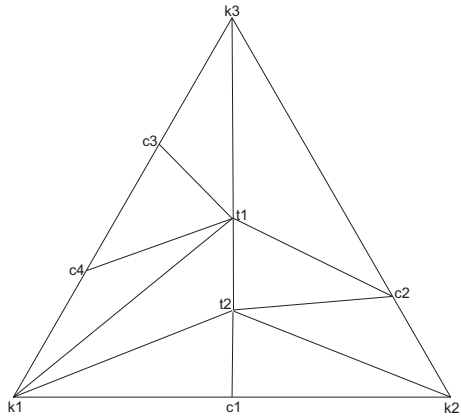

Figure 1. Example of triangulation.

To record the number of vertexes with different valence it is useful to use the formula $2^1 3^3 4^3 5^1 6^1$. It seems relevant to mention that $0 \le v_2 \le 3$.

To derive the formula of triangulation graphs it makes to apply the ratios (3). Thus, at $M = 1$, $N = 2$, one can find $f = 7$, $v = 6$, $v_{in} = 2$, $e = 11$, $e_{in} = 7$. In such a graph, the maximal valence of the vertex equals five. Therefore, the following equations $4v_2 + 3v_3 + 2v_4 + v_5 = 14$ and $2v_2 + v_3 + 0v_4 - v_5 = 2$ seem true. The formulae $3^2 4^4$, $3^3 4^2 5^1$, $3^4 5^2$, $2^1 3^1 4^3 5^1$, $2^1 3^2 4^1 5^2$ correspond to these ratios. Figure 2 shows eight possible triangulation schemes which correspond to these formulae.

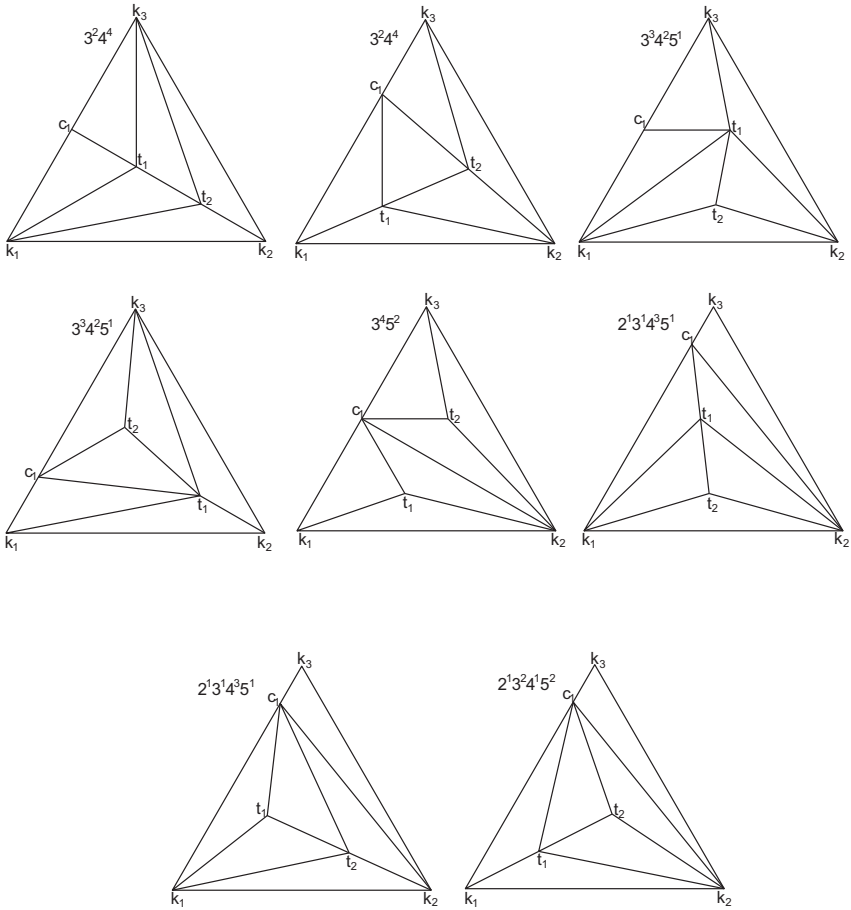

Figure 2. Triangulation graphs at $M = 1$, $N = 2$.

It is necessary to notice that the bivalent vertex corresponds to the component, while two other vertexes of the triangle in this case can correspond to either the second component and a binary compound or two binary compounds. It is obvious that the case when $v_2 = 3$ corresponds to the system without compounds or can be realized at $M \geq 3$ if the points of binary compounds lie on the three sides of the outline. The case $v_2 = 2$ can be realized at $M \geq 1$. The cases $v_2 = 1$ can be realized at $M \geq 1$ and $N \geq 1$.

Let any triangulation graph correspond to a planar graph with trivalent vertexes. To construct such a graph, one can add a new vertex outside the Gibbs triangle and joint it by the edges with other points of binary compounds. Next, construct a dual graph to the obtained graph. Each of such dual graphs presents a Schlegel projection of a polyhedron with trivalent vertexes on one of its faces. Figure 3 shows such a graph for triangulations $2^1 3^2 4^1 5^2$ given in Figure 2, which *per se* is a Schlegel projection of a polyhedron $3^2 4^3 6^2$ with two triangle, three quadrilateral, and two hexagonal faces.

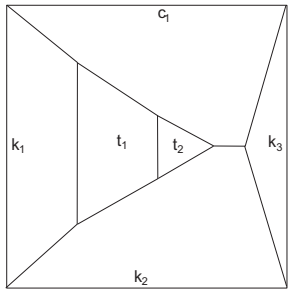

Figure 3. Dual graph for $2^1 3^2 4^1 5^2$ triangulation scheme which is a Schlegel projection of a $3^2 4^3 6^2$ polyhedron on the quadrangular face.

3. Typological classification and coding of triangulation schemes

The increase in the number of compounds in the system leads to a sharp increase in the number of possible triangulation schemes. To regulate such information it seems reasonable to classify triangulation schemes, which can be useful for the development of data compression and storage methods as well as construction of possible triangulation schemes. Since the most general characteristics of phase diagrams are of typological nature, it sounds reasonable to select triangulation schemes with the vertexes labeled by the symbols of the components and compounds or dual polyhedron graphs as the objects of classification. The large number of classification objects with various properties makes it necessary to create a hierarchical classification system. When choosing classification criteria for the upper levels,

it makes sense to focus on the basic chemical features of the system, while the taxons of the lower levels can be of purely topological nature. The classification of triangulation schemes given below is aimed at enumerating possible triangulation schemes and optimization of experimental building of such schemes.

To classify topological types of triangulation phase diagrams we suggest the following set of classification criteria.

1. *Code of compound (CC)*. From the set of ternary systems let's single out the type with the specified number of binary *M* and ternary *N* compounds. The sequence of these numbers *M*, *N* is called code of compounds.

2. *Code of boundary systems (CBS)*. Let's divide (*M, N*)-systems into the classes with different allocation of binary compounds on the sides of concentration triangle. The components are indicated by the symbols k_1, k_2 and k_3, while the binary compounds – c_i ($1 \le i \le M$). Code of boundary systems is formed from the component codes between which the symbols of binary compounds are located, for example, k_1k_2, $k_2c_1k_3$, $k_3c_2c_3k_1$. The combination of these records in ascending order of the number of binary compounds forms *CBS*, which consists of three symbols of the components and *M* symbols of binary compounds. For the given example $CBS = k_1k_2c_1k_3c_2c_3$.

3. *Code of vertexes valence (CVV)* shows the number of vertexes with different valence in a triangulation graph. It coincides with the formulae of the graphs given above, for example, $2^1 3^2 4^1 5^2$ for the graph in Figure 2.

4. *Code of triangulation* (*CT*) represents the enumeration of inner edges of triangulation graphs. They correspond to two-phase complexes (tie lines) of a ternary system. *CT* is recorded in the form of a succession $M + 3N$ of the pairs of symbols divided by the sign «/». We suggest using the following record order of tie lines' symbols. Let's choose in *CBS* the first vertex incidental to the inner edges of the triangulation graph and enumerate the symbols of these edges in a clockwise direction from the lateral of the outer triangle. Ternary compounds are indicated by the symbols t_j ($1 \le j \le N$); they are numbered in the order of occurrence of their symbols in *CT*. Repeat this procedure for the rest of the vertexes in *CBS*. As a result, the sequence of tie lines incident to the outer vertexes of the triangulation graph can be made. Next, in a lexicographical order one can record the sequence of tie lines joining the vertexes of ternary compounds.

To illustrate, let's consider classification characteristics of the triangulation scheme shown in Figure 1, where: $CC = 4, 2$; $CBS = k_1c_1k_2c_2k_3c_3c_4$; $CVV = 3^5 4^2 5^1 6^1$; $CT =$

$k_1t_1/k_1t_2/c_1t_2/k_2t_2/c_2t_2/c_2t_1/k_3t_1/c_3t_1/c_4t_1/t_1t_2$. It seems obvious that the set of the characteristics mentioned above is sufficient for a complete overall description of any triangulation graph.

4. Enumeration of topological types of phase diagram triangulations

The basis of enumeration algorithm is the above mentioned duality relation between triangulation schemes and cubic graphs of polyhedrons, which has made it possible to use the earlier created data base on polyhedrons with trivalent vertexes [9]. Suppose the number of M binary and N ternary compounds in a three-component system is specified.

1. Select all polyhedrons with the number of edges $M + N + 4$ containing the face $M + 3$ from the data base of simple polyhedrons [9]. Let's call each of such faces a component face and indicate it as k-face. For such a polyhedron one can form an automorphism group of and determine all nonequivalent k-faces.

2. For the selected k-face of a simple polyhedron P it is possible to create a code of vertexes valence which corresponds to the pair (P, k). Next, the list of all CVV values is made.

3. Three random edges of k-face are labeled by symbol 'k', while the rest M edges – by symbol 'c'. Lexicographically maximum word $W(k, c)$ specified by the condition: *'k' > 'c'* is made correspondent to the labeled k-face. This word is a code of boundary systems. Next, the list of all CBS values is made. Given the CBS, the set of all binary compounds is divided into three subsets with the number of compounds $m_1 \le m_2 \le m_3$, where m_1, m_2 and m_3 are the numbers of compounds in binary systems (k_1k_2), (k_2k_3) and (k_3k_1), correspondingly. After that, Schlegel diagram D of polyhedron P on k-face is made. Next, a geometrically dual graph to diagram D is constructed, where one vertex v_k corresponding to k-face is removed. As a result, one can obtain T ternary phase diagram triangulation; the vertexes are labeled as k_l, c_i and t_j. Finally, T triangulation code is created and the list of all CT is composed.

This algorithm makes it possible to generate the totality of topological triangulation schemes corresponding to the given set of classification characteristics. As a result, on the basis of this algorithm, the program has been developed. It is possible to define by this program, for example, that there are 244 schemes of topologically nonequivalent triangulations in the systems of three binary and two ternary compounds (CC – 3, 2), with 38 of them corresponding to the criterion ($CVV = 2^13^24^35^2$). Out of these 38 diagrams, 28 schemes correspond to the criterion ($CVV = k_1k_2c_1k_3c_2c_3$). Table 1 shows the number of nonequivalent triangulation schemes for the systems with different numbers of binary and

ternary compounds. Besides, the program makes it possible to look through topological schemes of all triangulations which correspond to the classification criteria.

Table 1. The number of nonequivalent triangulation schemes for the systems with different numbers of binary and ternary compounds.

M	*N*			
	0	1	2	3
0	1	1	1	4
1	1	2	8	38
2	2	10	50	293
3	6	37	244	1682

5. Optimization of experimental determination of triangulation in ternary phase diagrams

This task deals with planning experiments on the study of isothermal cross-sections of ternary phase diagrams. The researcher is supposed to be aware of the compositions of all binary and ternary compounds in the system and identify the presence of the components and compounds in experimental samples after reaching their equilibrium state. For the given set of binary and ternary compounds (i.e. parameters *CC* and *CBS*) there is a variety of triangulation options where only one corresponds to the equilibrium phase diagram. The idea of experiment planning is to define the number of samples and choose their total composition in order to determine the set of all stable binary and ternary associations of an equilibrium diagram with the minimal number of experiments. Optimization algorithms can be based on the choice of compositions of two-phase or three-phase samples or their combination.

The method suggested in [10] is based on constructing a complete graph of a subsolidus cross-section of a phase diagram with the specified vertexes coordinates. Next, out of the set of cross points of inner edges of a complete graph, the number of significant points is selected where the phase composition of the samples is determined experimentally. Finally, it is possible to determine which edge of the triangulation graph each point belongs to. The set of significant points should be sufficient for unambiguous creation of the scheme of a triangulation. To decrease the number of samples it makes sense to select significant points on the edges of a complete graph with the largest number of crossings. The method is efficient for the systems with a small number of compounds. However, it is difficult to apply this method at a large number of compounds. Besides, this method does not seem to determine, in an optimal way, the number of significant points sufficient for defining phase diagram triangulation. The suggested program which works in an interactive mode can easily solve these problems. When setting the task, the user inputs the number and composition of binary and ternary compounds existing in the system into the program. The program proposes the

user an optimal set of compositions of the samples for experimental study. The given set is sufficient for creating any possible triangulation which corresponds to the specified parameters of the system. Having determined experimentally the phase composition of the recommended samples, the user inputs these results into the program which defines the required triangulation.

The specific of the solution algorithm is as follows:

1. *Creating a complete graph.* The compositions of all binary and ternary compounds are specified. The points corresponding to these compositions are placed on the Gibbs triangle. Next, the graph is constructed, with the vertexes being the composition points of the compounds; each two points are jointed by the edge if and only if they don't lie on the one side of the Gibbs triangle. After that, label the constructed graph with the symbol *G*. The edges of graph *G* are considered as unlabeled. Finally, all the pairs of the intersecting edges are examined, the coordinates of crossing points are computed, and the list of these points is made. Let's label this set of points with P.

2. *The algorithm of creating a significant set.*

2.1. Let's call equilibrium $r(p_i)$ in the point p_i out of set P the list of phases on the end of the tie line which passes through this point or in the vertexes of one of the triangles in which this point is located. Let's call the list of equilibriums $r(p_1)$, $r(p_2)$,…$r(p_k)$ a contradictory one if there exists such an index i, which results in the lack of equilibrium $r(p_i)$ from equilibriums $r(p_1)$, $r(p_2)$,…$r(p_{i-1})$; otherwise, the list of equilibriums is called non-contradictory.

2.2. Let the subset of points $p_1,p_2,\ldots,p_k$ from P be called a significant one if, after removing from graph G all the edges crossing the edges which correspond to the specified equilibriums, for any list of non-contradictory equilibriums $r(p_1)$, $r(p_2)$,…$r(p_k)$, the obtained graph is a planar one.

2.3. From the set P a random point p_1 is selected. From graph G remove the edges crossing the edge which correspond to the specified equilibrium $r(p_1)$. If the obtained graph is a planar one, the significant set is considered as formed and consisting of the only point p_1. For the list of equilibriums $R=\{r(p_1), r(p_2),\ldots r(p_{k-1})\}$ let's call point p covered by this list if point p lies either on the edges of set R, or belongs to one of its triangles. Next, the significant set is added by point p_2 from P, which is not covered by the list of equilibriums $R=\{r(p_1)\}$. The given list is extended to $R=\{r(p_1),r(p_2)\}$. After that, the edges which cross the edges corresponding to the list of equilibriums R are removed from graph G. The last procedure is repeated unless the planar graph is obtained.

3. Algorithm of constructing triangulation on significant points.

3.1. For the selected (significant) point p two-phase or three-phase equilibrium r(p) is defined, which determines either the corresponding edge or a triangle. In graph G, the edges corresponding to the given equilibrium are labeled, while the crossing edges are removed.

3.2. The previous step is repeated unless a planar graph T – a required triangulation – is constructed.

To illustrate, let's consider phase diagram triangulation Li_2O-MoO_3-ZnO, where $M = 6$, $N = 1$; to construct such a phase diagram triangulation 27 samples were studied [11]. The use of the program has shown that the minimal number of samples sufficient for the solution of the given task equals 4.

6. Conclusion

The present classification together with the programs described above can be used in data bases on phase diagrams. The use of the experiment planning programs in the study of phase diagrams can significantly simplify the experimental construction of isothermal cross-sections of ternary phase diagrams with both phases of constant composition and limited solid solutions.

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