

# Triangulation of phase diagrams

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All possible triangulations of phase diagrams of ternary additive systems containing binary and ternary compounds were determined. It was assumed that all invariant points corresponding to ternary mixtures of basic components are eutectic in character and that all chemical compounds melt congruently. Further, the number of significant points was determined, *i.e.* the number of figurative points corresponding to ternary mixtures phase composition of which yields sufficient information for an unambiguous decision as to which of the possible triangulations exists in the given case.

Было определено число возможных триангуляций фазовых диаграмм трехкомпонентных аддитивных систем, содержащих двойные и тройные соединения в случае, когда все инвариантные точки, соответствующие тройным смесям основных компонентов систем имеют эвтектический характер и все химические соединения плавятся конгруэнтно. Далее, было определено число сигнификантных точек, т.е. число фигуративных точек, соответствующих тернарным смесям, фазовый состав которых представляет достаточную информацию для однозначного определения того, которая из возможных триангуляций реальна в данном случае.

Let us consider a ternary system A—B—C in which binary and ternary chemical compounds with congruently melting points are present. Let us assume that all reactions in this system have a eutectic character, *i.e.* all processes are of the type  $L \rightarrow A_s (B_s, C_s, M_s, \text{etc.})$ , where L is the liquid phase and  $A_s, B_s, C_s, M_s$  are the solid phases corresponding to substances A, B, C, M. Then from the point of general theory of phase diagrams and laboratory as well as technical praxis it is important to solve two basic problems:

1. In how many ways the triangulation of the system A—B—C can be realized, *i.e.* how this system can be divided into subsystems which do not contain any chemical compounds.

2. To determine the number of significant points of the basic ternary system A—B—C. This expression denotes the minimum number of figurative points of the

original ternary mixtures the phase composition of which allows to determine unambiguously which of the theoretically possible triangulations really exists.

For the first time the method for determination of triangulation of a system containing congruently melting binary compounds was described by *Guertler* [1]. The triangulation is discussed in several monographs on heterogeneous equilibria, e.g. [2—5]. However, until now, no general and systematic treatment of this problem has been given. It has not been stressed that the thermodynamic relationships for calculation of curves (or surfaces) of liquidus, based on the Le Chatelier—Shreder equation, may be used directly *only* for separate subsystems containing no chemical compounds. The triangulation is unevitable for the application of the Le Chatelier—Shreder equation in the complicated A—B—C system.

Let us have the system A—B—C which contains 3 binary compounds Q, M, N (Fig. 1). Then there exist 5 internal diagonals, i.e. lines connecting figurative points A, B, C, Q, M, N which intersect mutually in three points,  $P_1, P_2, P_3$ . In order to determine which of the triangulations *a, b, c* is the true one we have to determine the phase composition of the mixtures corresponding to points  $P_1, P_2, P_3$ . Let us analyze each of the points  $P_1, P_2, P_3$ .

Point  $P_1$ : The phase analysis of the cooled system with a composition corresponding to the point  $P_1$  shows either the presence of solid phases A and Q (we shall describe it as  $P_1(A, Q)$ ) or C and M ( $P_1(C, M)$ ).

In the case  $P_1(A, Q)$  the diagonal A—Q is stable, i.e. the independent elementary system A—C—Q can be detached from the system A—B—C. There remains the system A—B—Q with binary compounds M, N with figurative points lying on the abscissa A—B. Then its triangulation can be done only in a single way, namely by creating the elementary systems A—M—Q, M—N—Q, and N—B—Q. Therefore, the case  $P_1(A, Q)$  implies  $P_2(M, Q)$  and the triangulation is unambiguous.

In the case  $P_1(C, M)$  we can detach the ternary system A—C—M and the triangulation of the remaining system B—C—M can be realized in two ways. Either

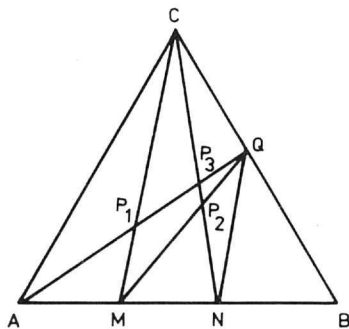


Fig. 1. System with two compounds of substances A and B and one compound of substances B and C.

it holds  $P_2(C, N)$  and then the elementary systems are  $C-M-N$ ,  $C-N-Q$ ,  $B-Q-N$ , or it holds  $P_2(M, Q)$  and then the elementary systems are  $C-M-Q$ ,  $M-N-Q$ ,  $B-Q-N$ . Therefore, the triangulation in the case  $P_1(C, M)$  is not determined unambiguously. It is to be pointed out that for the point  $P_1$  there are only the two possibilities discussed above.

Point  $P_2$ : It is easy to show that it holds either  $P_2(C, N)$ , which implies  $P_1(C, M)$ , and the triangulation is unambiguous, or  $P_2(M, Q)$ , which implies two possibilities:  $P_1(A, Q)$  or  $P_1(C, M)$ . The case  $P_2(M, Q)$  leads again to an ambiguous situation. Therefore, for the point  $P_2$  it has to occur just one of the described situations.

Point  $P_3$ : There are three possibilities in this case:

a) It holds  $P_3(A, Q) \Rightarrow P_2(M, Q)$ , which corresponds to the unambiguous triangulation  $A-Q-C$ ,  $A-M-Q$ ,  $M-N-Q$ , and  $B-Q-N$ .

b) It holds  $P_3(C, N) \Rightarrow P_1(C, M)$ , which corresponds to the unambiguous triangulation  $A-M-C$ ,  $M-N-C$ ,  $N-Q-C$ , and  $B-Q-N$ .

c) It holds that the point  $P_3$  does not lie on any stable diagonal (thus the phase composition of a mixture corresponding to this point contains three and not two compounds as in the cases a) and b), namely  $C, M, Q$ ). This situation corresponds to unambiguous triangulations  $A-M-C$ ,  $C-M-Q$ ,  $M-N-Q$ , and  $B-M-Q$ .

Phase composition of the ternary mixture corresponding to point  $P_3$  determines unambiguously which of the theoretically possible triangulations is real. Therefore, the point  $P_3$  is the significant point in the system  $A-B-C$ . It is the only point with this property.

From the practical point of view it is important that the cases a–c distinguish markedly in the phase composition of cooled mixtures, which makes the determination of the real triangulation easier.

Each of the triangulations shown in Fig. 2a–c contains the same number of elementary triangles. We shall prove that this number of elementary triangles is for the given system constant and that it does not depend on the position of figurative points of compounds but only on the number of these points. The system containing no chemical compound (binary or ternary) can be figured by one

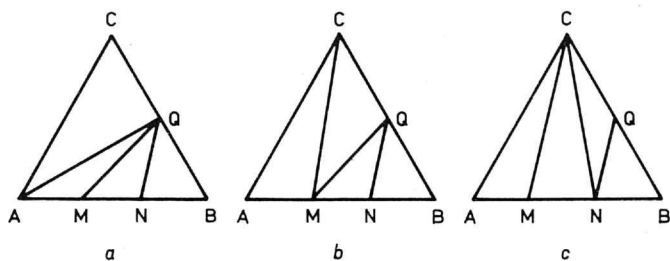


Fig. 2. Triangulations of the system presented in Fig. 1.

triangle. Adding a binary compound on one side of the triangle increases the number of elementary triangles by one. The addition of a ternary compound with a figurative point lying within the triangle increases the number of elementary triangles by two. The system with  $n_1$  binary and  $n_2$  ternary compounds can be imagined as a result of subsequent addition of figurative points to the basic triangle. It follows that the total number of elementary triangles in the diagram,  $N$ , is given as

$$N = 1 + n_1 + 2n_2$$

The problem to determine the number of triangulations is somewhat more complicated. In the beginning we shall restrict our considerations to the systems containing binary compounds only.

### *Systems with binary compounds*

In our considerations we shall assume three basic components A, B, C and their binary compounds. The compounds of substances A, B are denoted as  $P_i$ , the compounds of substances B, C as  $Q_j$  and those of substances A, C as  $R_k$ . The number of triangulations of the system containing  $p$  substances  $P_i$ ,  $q$  substances  $Q_j$ , and  $r$  substances  $R_k$  will be denoted as  $N(p, q, r)$ .

Relatively simple situation is in systems with only two binary compounds, e.g. of the type  $P_i$  or  $Q_j$ . If there are in the system compounds of one type, there is only one possible triangulation. For the initial values of the function  $N(p, q, r)$  we obtain

$$N(p, 0, 0) = 1$$

$$N(0, q, 0) = 1$$

$$N(0, 0, r) = 1$$

Let us further assume that the system contains substances of two kinds (Fig. 3). From the character of the diagram it follows that the diagonals A— $Q_q$  and C— $P_1$

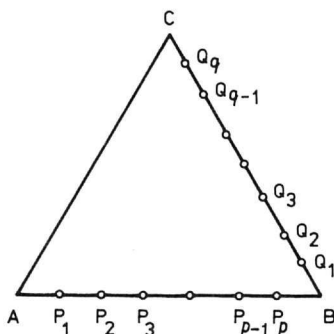


Fig. 3. System with two types of binary compounds.

cannot exist simultaneously in any real system. Therefore, all theoretically possible triangulations can be divided into two groups

I — triangulations with the diagonal A—Q<sub>q</sub>,

II — triangulations with the diagonal C—P<sub>1</sub>.

The number of triangulations in the first group is  $N(p, q - 1, 0)$  and the number of triangulations in the second group is  $N(p - 1, q, 0)$  because in the first case there remain yet  $p$  compounds P<sub>i</sub> and  $q - 1$  compounds Q<sub>j</sub>. Similar reasoning can be used in the second case.

Therefore, the total number of triangulations is

$$N(p, q, 0) = N(p, q - 1, 0) + N(p - 1, q, 0)$$

Because it holds  $N(p, 0, 0) = 1$  and  $N(0, q, 0) = 1$ , we can always find the number  $N(p, q, 0)$  using a finite number of operations. The quantities  $N(p, q, 0)$  are arranged in Table 1.

Table 1  
Values of the function  $N(p, q, 0)$

| $p$ | $q$ |   |    |    |    |
|-----|-----|---|----|----|----|
|     | 0   | 1 | 2  | 3  | 4  |
| 0   | 1   | 1 | 1  | 1  | 1  |
| 1   | 1   | 2 | 3  | 4  | 5  |
| 2   | 1   | 3 | 6  | 10 | 15 |
| 3   | 1   | 4 | 10 | 20 | 35 |
| 4   | 1   | 5 | 15 | 35 | 70 |

The result can be expressed in a condensed form by means of combination numbers. The number  $\binom{m}{n}$  is defined as follows

$$\binom{m}{n} = \frac{m(m-1)(m-2)\dots(m-n+1)}{n(n-1)(n-2)\dots 1}$$

The number of theoretically possible triangulations is given as

$$N(p, q, 0) = \binom{p+q}{p} = \binom{p+q}{q}$$

This abbreviated notation as well as the calculation will be used also in further considerations. In a similar way can be determined also

$$N(0, q, r) = \binom{q+r}{q} \quad \text{and} \quad N(p, 0, r) = \binom{p+r}{r}$$

This result will be specially useful in the investigation of the systems containing binary compounds of all three types. If a triangulation contains the diagonal  $A-Q_j$  then it cannot contain either the diagonal  $B-R_k$  or the diagonal  $C-P_i$ . We shall divide all triangulations into four mutually nonoverlapping groups

I — triangulations containing diagonals of the type  $A-Q_j$ ,

II — triangulations containing diagonals of the type  $B-R_k$ ,

III — triangulations containing diagonals of the type  $C-P_i$ ,

IV — triangulations which do not contain any of the diagonals mentioned above.

If we determine the number of triangulations in each group the total number of theoretical triangulations equals the sum of triangulations in single groups.

Let us determine the number of triangulations which contain the diagonals of the type  $A-Q_j$  for  $1 \leq j \leq q$ . If there are more diagonals of this type in a triangulation we can find indices  $j_1$  and  $j_2$  in such a way that  $j_1$  is the minimum and  $j_2$  the maximum index with this property, so that the diagonals  $A-Q_{j_1}$  and  $A-Q_{j_2}$  belong to the given triangulation. If there are  $q_B$  compounds between substance B and compound  $Q_{j_1}$  and  $q_C$  compounds between substance C and compound  $Q_{j_2}$  then the original system can be divided into two simpler systems (Fig. 4). The number of triangulations in such a part of the system can be expressed in a similar way as in the preceding part

$$N(p-1, q_B, 0) N(0, q_C, r-1)$$

For the total number of triangulations in the group I it holds

$$N_I = \sum_{q_C + q_B \leq q-1} N(p-1, q_B, 0) N(0, q_C, r-1)$$

In a similar way we can obtain the number of triangulations in the groups II and III

$$N_{II} = \sum_{p_A + p_B \leq p-1} N(p_A, 0, r-1) N(p_B, q-1, 0)$$

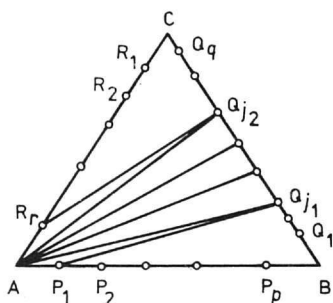


Fig. 4. Triangulation with a diagonal containing the basic substance.

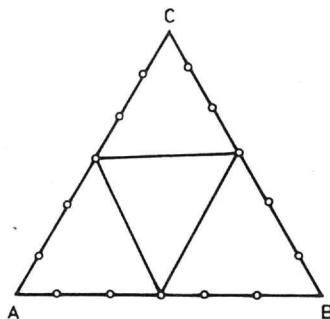


Fig. 5. Triangulation containing an internal triangle.

$$N_{\text{III}} = \sum_{r_A + r_C \leq r-1} N(p-1, 0, r_A) N(0, q-1, r_C)$$

It remains to determine the number of triangulations in the group IV. Each of these triangulations includes the triangle of the type  $P_i-Q_j-R_k$  and it splits into three simple systems (Fig. 5). The number of triangulations in the group IV is given as

$$N_{\text{IV}} = \sum_{\substack{p_A + p_B = p-1 \\ q_C + q_B = q-1 \\ r_C + r_A = r-1}} N(p_A, 0, r_A) N(p_B, q_B, 0) N(0, q_C, r_C)$$

In all cases the summation is carried out over all indices given by inequalities under the sign of the sum. The total number of triangulations in the system containing binary compounds is given as

$$N = N_{\text{I}} + N_{\text{II}} + N_{\text{III}} + N_{\text{IV}}$$

### Systems with binary and ternary compounds

In the case when the system contains both binary and ternary compounds the theoretically possible number of triangulations depends on geometrical position of figurative points of the compounds. First we shall investigate the case of two compounds in the system. If both figurative points lie on the abscissa passing through any of the points A, B, C there exists just one triangulation (Fig. 6).

If the figurative points lie in a general position with respect to the points A, B, C then there exist just two theoretically possible triangulations (Fig. 7). The diagonals which cannot belong simultaneously to both triangulations are drawn with dashed lines.

Situation is more complicated in a system containing three compounds. This case may be divided into three groups.

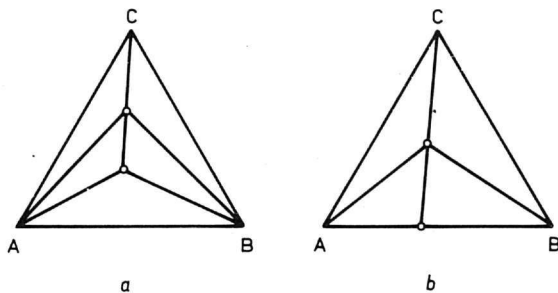


Fig. 6. The case of two compounds which lie on one diagonal.

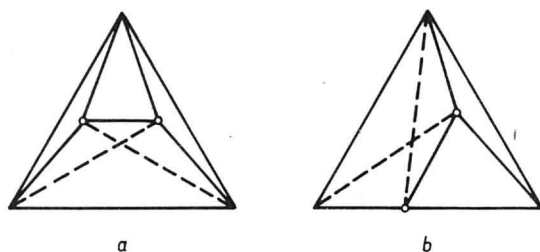


Fig. 7. System with two compounds in general position.

1. There are one binary and two ternary compounds in the system. Then eight cases of geometrical position of figurative points can occur. These cases are demonstrated in Fig. 8.

The case *a*) allows only one triangulation.

The case *b*) allows two triangulations.

The case *c*) allows three triangulations.

The cases *d*) and *e*) allow four triangulations.

The cases *f*), *g*), and *h*) allow five triangulations.

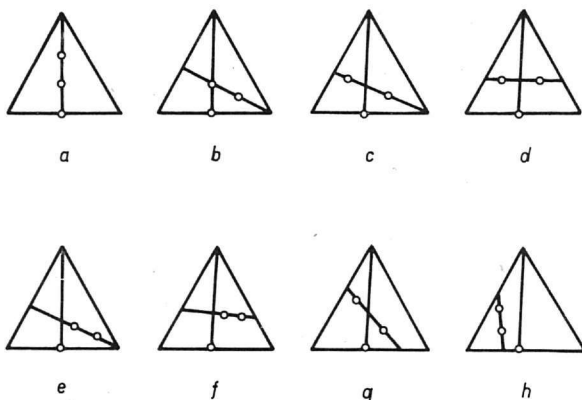


Fig. 8. Systems with two ternary and one binary compounds.

2. There are two binary and one ternary compounds in the system. Then nine cases can occur, which depends on the geometrical position of figurative points. All possible cases are demonstrated in Fig. 9.

The case *a*) allows only one triangulation.

The case *b*) allows two triangulations.

The cases *c*) and *d*) allow three triangulations.

The cases *e*), *f*), and *g*) allow four triangulations.

The cases *h*) and *i*) allow five triangulations.



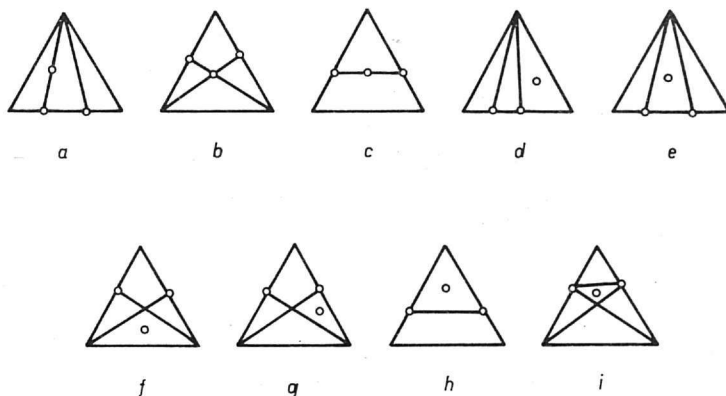


Fig. 9. Systems with two binary and one ternary compounds.

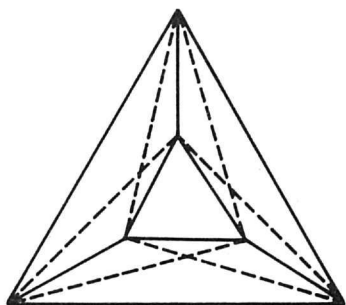


Fig. 10. Example of the system with three ternary compounds.

3. There are three ternary compounds in the system. In this case there can be one to eight triangulations according to the geometrical position of figurative points. For illustration, we shall present the case of the system with eight possible triangulations (Fig. 10). The diagonals which cannot be in all triangulations are drawn in dashed line. Choosing one of the dashed lines which intersect we obtain eight different triangulations of the system.

#### *Sets of significant points*

For the applicability of the method of triangulation of phase diagrams it is important to determine effectively the type of triangulation which occurs in the given case. The set of figurative points the phase analysis of which is sufficient for determination of triangulation will be called the set of significant points. For the sake of brevity we are looking for a minimum set of significant points. It is the set from which no point can be omitted without breaking its crucial property. We shall show a general method for finding the significant set of points and we shall illustrate this method on a special example.

On the basis of the preceding parts we know that the system corresponding to the diagram in Fig. 11 allows eight triangulations. We shall find the set of points which will be significant. There are 14 points of intersection of diagonals within the triangle A—B—C. From this set of points it is possible to find a significant one. To the system shown in the figure the graph can be found in the following way: The intersections of diagonals will be chosen as vertices of the graph (14 vertices in our case). Two vertices in the graph will be neighbouring, *i.e.* connected by an edge, if the corresponding points lie on the same diagonal. The set of significant points is then determined by the minimum set of vertices covering the graph. It means that each vertex in the graph corresponds to a significant point or is connected with such a point by means of an edge. We can find this minimum set in a relatively simple way. The application of the algorithm will be demonstrated directly in the diagram.

First step: We choose the intersection which lies on the diagonals with a maximum number of points (in the language of graphs the vertex of the highest degree). In our case it is the point 7. If there are more points with this property we choose arbitrarily one of them.

Second step: We shall mark the chosen vertex (*e.g.* with red colour) in order to distinguish it from other points in the diagram. The points which lie on the common diagonal with the point 7 are to be marked in another way (*e.g.* with blue colour).

Third step: Similarly as in the first step we choose one of unmarked points (*e.g.* the point 9 in our case) and we paint it red. All other points which are on the same diagonal should be painted blue.

Fourth step: From the set of the until now uncoloured points we choose a further point — the point 5. All other points are blue, the point 5 is red.

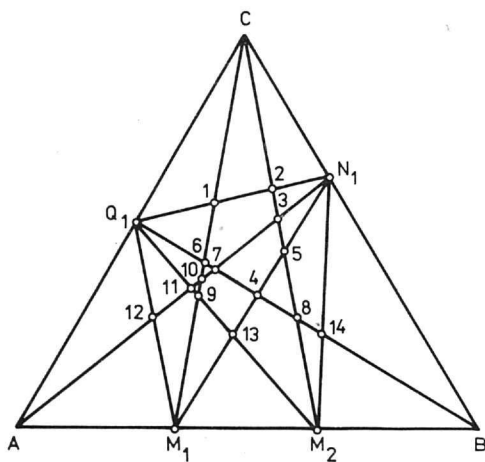


Fig. 11. System with four binary compounds. Intersection points are illustrated.

When all intersection points are coloured, the algorithm is finished. The set of red points is the minimum set of significant points. Those are the points 7, 5, 9 in our example.

Therefore, for unambiguous determination of a real triangulation of the given system it is sufficient to carry out the phase analysis of mixtures corresponding to the figurative points 5, 7, and 9.

From the presented algorithm it is obvious that the set of significant points is not necessarily determined unambiguously. There can exist therefore more sets of significant points. The sets of significant points can be found using the algorithm presented in [6].

The example which was used for illustration of the utilization of the algorithm was applied to the system with binary compounds. However, it is easy to understand that it can be used in arbitrary ternary system containing both binary and ternary compounds.

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