Polyhedronization of concentration figures of phase diagrams of four-component systems

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The problems of polyhedronization of concentration tetrahedron of a four-component additive system forming an arbitrary number of binary congruently melting compounds are solved by means of geometric analysis. The case when the figurative points of these compounds lie on not more than three edges of the concentration tetrahedron is treated. Solution for all six alternatives of this case is presented. A method for determination of significant points of the polyhedronization is presented as well.

С помощью геометрического анализа решена проблема полиэдризации концентрационного тетраэдра четырехкомпонентной системы, содержащей произвольное число бинарных соединений с конгруэнтной точкой плавления. Был рассмотрен случай, когда фигуративные точки этих соединений расположены максимум на трех гранях концентрационного тетраэдра. Приведено решение для всех шести возможных вариантов. Показан способ определения сигнификантных точек полиэдризации.

Let us consider a k-component condensed system of the type A—B—C ... —K at constant pressure. Let us suppose that there are in the system congruently melting complex compounds of the type A_aB_b, $A_aB_bC_c$, ..., $A_aB_b \dots K_k$. Let us further suppose that all processes in the system, which take part in phase equilibria, have eutectic character. It means that the solid phases formed do not further change by decrease of temperature.

Then it is always possible to divide the original complicated system to a certain number of systems having simple eutecticum. This procedure is called polyhedronization and it simplifies remarkably experimental and theoretical study of the complicated systems.

The polyhedronization is related to the concentration figure which represents the given system. From the geometrical point of view there are more possibilities how to do a polyhedronization but only one case corresponds to physical reality. From this point of view it is important to find out the number of necessary pieces of information needed for unambiguous determination of physically real polyhedronization. The information is related to the phase composition of particular systems corresponding to certain figurative points which we denote as significant points. Generally there are more sets of significant points. For practical purpose it is useful to find out that which is the smallest one.

The simplest case of the above-mentioned problem has been solved for the first time by *Guertler* [1] and it is discussed in monographs [2, 3]. In paper [4] we presented general solution of this problem for ternary systems. In this paper we deal with some types of quaternary systems.

Preliminary considerations and supporting calculations

We assume that there is given a system of four basic substances (components) which form only binary compounds. Concentration polyhedron of the system is a regular tetrahedron the vertexes of which correspond to the components. Figurative points of binary compounds, which are formed by the components, lie on edges of the tetrahedron. Assuming that all components in the system melt congruently the tetrahedron can be divided to elementary concentration figures which are again tetrahedrons.

Division of the basic tetrahedron to the elementary tetrahedrons can be unambiguously described by projections of dividing planes on surfaces of the tetrahedron. Each projection is a triangle and therefore it is useful to derive also relations describing the number of possible triangulations of concentration triangle and to present corresponding tables for a three-component system.

Number of triangulations of the triangle ABC which contains p compounds of substances A and B, q compounds of B and C, and r compounds of C and A will be denoted as $P(p, q, r)$. For the numbers $P(p, q, r)$ it holds

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

$$P(p, 0, r) = \binom{p+r}{p} = \binom{p+r}{r}$$

$$P(0, q, r) = \binom{q+r}{r} = \binom{q+r}{q}$$

In the case that all the parameters p, q, and r differ from zero, it holds

$$P(p, q, r) = \sum_{p_1+p_2=p-1} \binom{p_1+r-1}{r-1}\binom{p_2+q-1}{q-1} + \\ + \sum_{r_1+r_2=r-1} \binom{r_1+q-1}{q-1}\binom{r_2+p-1}{p-1} + \\ + \sum_{q_1+q_2=q-1} \binom{q_1+p-1}{p-1}\binom{q_2+r-1}{r-1} + \\ + \sum_{\substack{r_1+r_2=r-1\\ p_1+p_2=p-1\\ q_1+q_2=q-1}} \binom{p_1+r_2}{p_1}\binom{p_2+q_1}{q_1}\binom{r_1+q_2}{r_1}$$

where p_1, p_2, q_1, q_2, r_1, r_2 are nonnegative numbers.

Table 1

Number of possible triangulations of the basic concentration triangle of the ternary system A—B—C calculated for the case when in the system p binary compounds of the type A_xB_y and q binary compounds of the type B_xC_y are formed
p and q change in the interval 0—5

q	p = 0	1	2	3	4	5
0	1	1	1	1	1	1
1	1	2	3	4	5	6
2	1	3	6	10	15	21
3	1	4	10	20	35	56
4	1	5	15	35	70	126
5	1	6	21	56	126	252

Table 2

Number of possible triangulations of the basic concentration triangle of the ternary system A—B—C calculated for the case when in the system p binary compounds of the type A_xB_y, q binary compounds of the type B_xC_y, and one ($r = 1$) binary compound of the type A_xC_y are formed

q	p = 0	1	2	3	4	5
0	1	2	3	4	5	6
1	2	4	7	11	16	22
2	3	7	14	25	41	63
3	4	11	25	50	91	154
4	5	16	41	91	182	336
5	6	22	63	154	336	672

Table 3

Number of possible triangulations of the basic concentration triangle of the ternary system A—B—C calculated for the case when in the system p binary compounds of the type A_xB_y, q binary compounds of the type B_xC_y, and two ($r=2$) binary compounds of the type A_xC_y are formed

q	p					
	0	1	2	3	4	5
0	1	3	6	10	15	21
1	3	7	14	25	41	63
2	6	14	29	55	97	161
3	10	25	55	111	209	371
4	15	41	97	209	419	791
5	21	63	161	371	791	1583

Table 4

Number of possible triangulations of the basic concentration triangle of the ternary system A—B—C calculated for the case when in the system p binary compounds of the type A_xB_y, q binary compounds of the type B_xC_y, and three ($r=3$) binary compounds of the type A_xC_y are formed

q	p					
	0	1	2	3	4	5
0	1	4	10	20	35	56
1	4	11	25	50	91	154
2	10	25	55	111	209	371
3	20	50	111	229	446	826
4	35	91	209	446	901	1737
5	56	154	371	826	1737	3485

Table 5

Number of possible triangulations of the basic concentration triangle of the ternary system A—B—C calculated for the case when in the system p binary compounds of the type A_xB_y, q binary compounds of the type B_xC_y, and four ($r=4$) binary compounds of the type A_xC_x are formed

q	p					
	0	1	2	3	4	5
0	1	5	15	35	70	126
1	5	16	41	91	182	336
2	15	41	97	209	419	791
3	35	91	209	446	901	1737
4	70	182	419	901	1847	3639
5	126	336	791	1737	3639	7333

Table 6

Number of possible triangulations of the basic concentration triangle of the ternary system A—B—C calculated for the case when in the system p binary compounds of the type A_xB_y, q binary compounds of the type B_xC_y, and five ($r = 5$) binary compounds of the type A_xC_y are formed

q	p					
	0	1	2	3	4	5
0	1	6	21	56	126	252
1	6	22	63	154	336	672
2	21	63	161	371	791	1584
3	56	154	371	826	1737	3485
4	126	336	791	1737	3639	7333
5	252	672	1584	3485	7333	14952

The above formula does not provide an easy survey. Tables 1—6 present the values of the function $P(p, q, r)$ for small integers p, q, r.

Division of the basic tetrahedron into elementary tetrahedrons

Now we shall deal with the question of the number of ways in which the tetrahedron ABCD containing binary compounds of substances A, B, C, and D can be divided. We shall limit discussion to those cases when the figurative points of the compounds are not distributed on more than three edges of the tetrahedron. All the cases which can occur are following:

— all compounds are situated on one edge;
— all compounds are situated on two neighbour edges;
— all compounds are situated on two opposite edges;
— all edges on which the binary compounds lie originate in the same vertex;
— all edges on which the binary compounds lie are in the same plane;
— the compounds lie on three edges which have just two common vertexes.

1. All compounds are situated on one edge

If all compounds are concentrated on one edge, then only one way of the division of the basic tetrahedron to elementary tetrahedrons exists (Fig. 1).

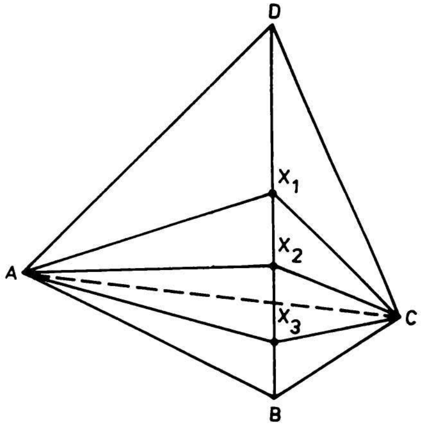

Fig. 1. Concentration tetrahedron of the system A—B—C—D with binary compounds the figurative points of which lie on the edge BD.

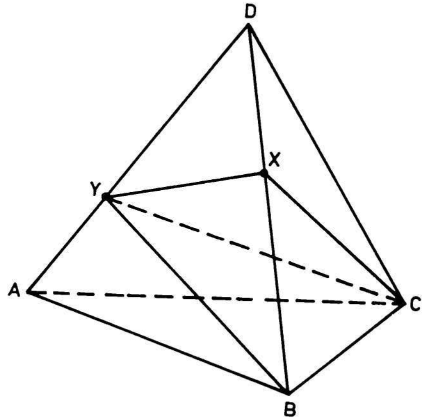

Fig. 2. Concentration tetrahedron of the system A—B—C—D. Two binary compounds X and Y lie on two neighbour edges of the tetrahedron (*i. e.* these edges have a common vertex).

2. All compounds are situated on two neighbour edges

If all compounds are situated on two neighbour edges, then it holds that the number of divisions into elementary tetrahedrons equals

$$N(x, y) = \binom{x+y}{x} = \binom{x+y}{y}$$

It follows that the division into tetrahedrons determines unambiguously the division of triangle into elementary triangles. And oppositely, if we have a division of the basic triangle, we know projections of the dividing planes and the division of the tetrahedron is therefore determined unambiguously (Fig. 2).

3. All compounds are situated on two opposite edges

If all compounds are situated on two opposite edges, each surface of the triangle allows only one triangulation. Therefore, there exists only one division of the basic tetrahedron into elementary tetrahedrons (Fig. 3).

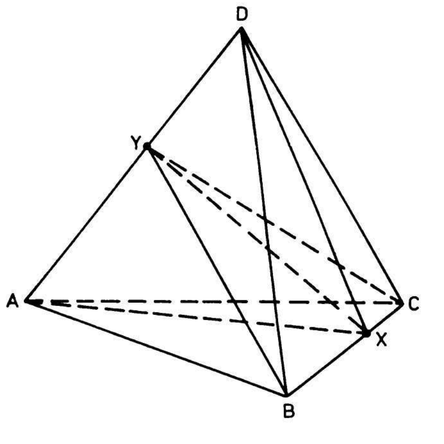

Fig. 3. The case of the quaternary system A—B—C—D with binary compounds the figurative points of which are situated on two opposite edges of concentration tetrahedron (*i. e.* these edges have not a common vertex).

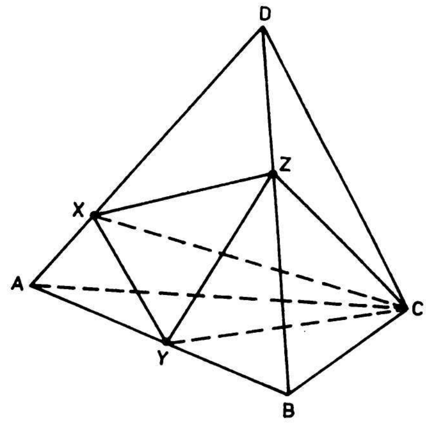

Fig. 4. The case of the quaternary system A—B—C—D with binary compounds the figurative points of which are situated on one surface of concentration tetrahedron.

4. All edges on which the binary compounds lie originate in the same vertex

Let us suppose that compounds are on three edges which originate in the vertex A and their numbers are x, y, z. Let us denote $P(x, y, z)$ the number of divisions of tetrahedron into elementary tetrahedrons. Then it holds

$$P(x, y, z) = P(x-1, y, z) + P(x, y-1, z) + P(x, y, z-1) \qquad (1)$$

Simultaneously it holds for all integers x, y, z

$$P(x, 0, 0) = P(0, 0, z) = P(0, y, 0) = 1 \qquad (2)$$

The relations (*1*) and (*2*) determine unambiguously the integer function P. If we express the function P in explicit form we obtain

$$P(x, y, z) = \frac{(x+y+z)!}{x!\,y!\,z!} = \binom{x+y+z}{x,\ y,\ z}$$

The function $\binom{x+y+z}{x,\ y,\ z}$ has analogical properties as binomial coefficients. The numbers $\binom{n}{n_1,\ n_2,\ n_3}$ are called trinomial coefficients ($n_1 + n_2 + n_3 = n$). In Tables 7—10 the values of trinomial coefficients are presented for n ranging from 0 to 5.

5. All edges on which the binary compounds lie are in the same plane

In this case the triangulation of the basic triangle, which contains all compounds, determines unambiguously division of the basic concentration tetrahedron of phase diagram into elementary tetrahedrons. Numbers of different triangulations are presented in the former paragraph. Triangulations of the other surfaces of the tetrahedron are also determined unambiguously. As follows from Fig. 4, they result from projection of dividing planes.

Table 7

Values of trinomial coefficients $\binom{n}{n_1,\, n_2,\, n_3}$

$n_1 = 0$

n_3	n_2					
	0	1	2	3	4	5
0	1	1	1	1	1	1
1	1	2	3	4	5	6
2	1	3	6	10	15	21
3	1	4	10	20	35	56
4	1	5	15	35	70	126
5	1	6	21	56	126	252

Table 8

Values of trinomial coefficients $\binom{n}{n_1,\, n_2,\, n_3}$

$n_1 = 1$

n_3	n_2					
	0	1	2	3	4	5
0	1	2	3	4	5	6
1	2	6	12	20	30	42
2	3	12	30	60	105	168
3	4	20	60	140	280	504
4	5	30	105	280	630	1260
5	6	42	168	504	1260	2772

Table 9

Values of trinomial coefficients $\binom{n}{n_1,\, n_2,\, n_3}$

$n_1 = 2$

n_3	n_2					
	0	1	2	3	4	5
0	1	3	6	10	15	21
1	3	12	30	60	105	168
2	6	30	90	210	420	756
3	10	60	210	560	1260	2520
4	15	105	420	1260	3150	6930
5	21	168	756	2520	6930	16632

Table 10

Values of trinomial coefficients $\binom{n}{n_1,\, n_2,\, n_3}$

$n_1 = 3$

n_3	n_2					
	0	1	2	3	4	5
0	1	4	10	20	35	56
1	4	20	60	140	280	504
2	10	60	210	560	1260	2520
3	20	140	560	1680	4200	9240
4	35	280	1260	4200	9660	29830
5	56	504	2520	9240	25830	68292

6. The compounds lie on three edges which have just two common vertexes

If all compounds lie on three edges of the basic tetrahedron and these edges have just two common vertexes, then there are two surfaces of the tetrahedron which can be triangulated in different ways. In the case which is illustrated in Fig. 5, these surfaces are ABD and BCD. Their triangulation determines unambiguously division of the basic tetrahedron into elementary tetrahedrons. It is to be decided which of the two diagonals AY and BX in the surface ABD is stable. It is equivalent to the question which of two geometrically possible triangulations

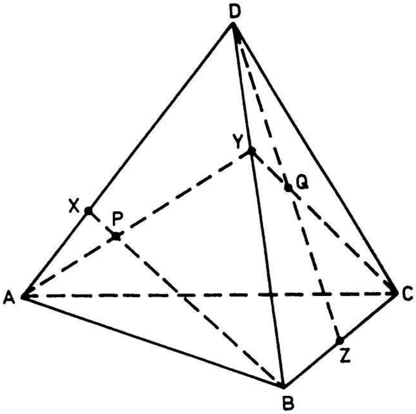

Fig. 5. The case of the quaternary system A—B—C—D with binary compounds the figurative points of which lie on three edges of concentration tetrahedron. These edges have two common vertexes, *viz.* B and D. P and Q are the significant points.

corresponds to physical reality. This problem can be solved only by experiment. Decisive role plays phase composition of the system at the point P. Thus this point is called to be significant. Similar law holds also for the surface BCD. In this case Q is the significant point. Total number of divisions of the tetrahedron can be expressed in the form of the following equation

$$P(x, y, z) = \binom{x+y}{y}\binom{y+z}{y}$$

where x, y, z are the numbers of binary compounds on edges of tetrahedron; y corresponds to the edge which has the common vertex with the remaining two edges. In the case illustrated in Fig. 5, there are four different ways of division of the basic tetrahedron into elementary tetrahedrons.

Significant points

Similarly as in the case of division of triangle it is important to know which particular polyhedronization is relevant to our real system. We can find out this polyhedronization on the basis of the phase analysis of substances which correspond to significant points. These points are placed on the interceptions of the diagonals of triangles. In the case of polyhedronization of tetrahedrons the figurative points of substances are distributed in the way which has been discussed above. Thus it is necessary to investigate significant points which lie on surfaces of tetrahedron and which allow different triangulations. *E.g.* in the case given in Fig. 5 there are two significant points P and Q. From phase analysis of mixtures corresponding to these points one can find out which of the four possible divisions can be applied to our system.

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