Topological Correction of Multicomponent Systems

Polyhedration

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Abstract. An algorithm (Topological Correction of Lists of Simplexes of Different Dimensions) for polyhedration of quaternary reciprocal systems is presented. It can control all polyhedration stages, accelerates the search of internal diagonals and takes into account their possible competition.

1. Introduction

Melting Salt Reactor is one of the concepts of the IV generation nuclear reactors with the molten salt fuel compositions. According to the rules of selection, the preferable salt compositions are the metal fluorides. Nevertheless, despite the fact that the chloride’s systems have a high vapor pressure and low thermodynamic stability at high temperatures than the fluoride’s ones, they are less aggressive in relation to the structure of the material and have lower melting points. However, they can be used only in the fast reactors, but not in the thermal ones. Therefore, in order to ensure reliable operation of new generation reactors the comprehensive information on equilibria and chemical processes in the reciprocal fluoride-chloride systems are to be provided. One of the necessary conditions for the implementation of a nuclear power new generation is to detect the regularities, which permit to predict the change of physical and chemical properties of fluoride-chloride systems with the accumulation of products of nuclear transformations. Such regularities are preferable to extract from the information on the phase equilibria accumulated in the multidimensional phase diagrams of these systems [1].

Phase diagrams of reciprocal systems are a special class among others, because the concentration base is not a simplex, but a complex. Known calculate methods and phase diagrams simulation programs are developed mainly for the simplexes (triangles, tetrahedra, …). Therefore, the main questions are the correct concentration coordinate system [2], and the polyhedration or dividing the concentration complex into the energetically stable subsystems.

2. Polyhedration of multicomponent systems

Polyhedration of a multicomponent system is very important stage of its investigation because it can minimize the experimental data. In this case, it is generally unknown (or only partially known) what phases are formed inside the system, as well as the information on the boundary systems may be incomplete or wrong. If the system is studied completely, the meaning of polyhedration is to check the consistency of triangulation of its faces and also to pass to the prediction of new variants of polyhedration at other temperatures and pressures.

2.1. Polyhedration algorithms

Usually the reciprocal system concentration complex has been shown as a graph and it is described by the adjacency matrix. Known algorithms are based on graph decomposition by or the adjacency matrix zero elements (the missing links between vertices), or, on the contrary, by the unit elements, that correspond to the connected graph vertexes. Such algorithms are widely used in practice and often
cited (see, e.g., [3,4]). The software for multicomponent systems polyhedration was created [5]. It is based on the graph decomposition by the multiplying of adjacency matrix zero elements on the law of absorption and inversion of its result.

The problem occurs if the adjacency matrix contains unknown elements, when we do not know, whether there are links between the graph vertices or not. As all links between the graph vertices in boundary systems are known before the polyhedration, internal diagonals remain mainly unknown. In some cases they may be found without great problems. So, you can use the decomposition algorithm for the graph, simply sorting out the possible links between the vertices of the graph, which could become the internal diagonals. There are also the methods, using “matrixes of vertices indexes” and “metathesis reactions analysis” to identify internal diagonals [3,4].

The newly developed algorithm is based on the topological correction of the lists for the simplexes of different dimension (TCLSDD) [6,7]. It is based on the scanning of all the relationships between the vertices of the graph that describes the concentration complex and selecting those variants of polyhedration, which correspond to the ratios between the quantities of different geometrical elements within the investigated complex (vertices of the graph, the links between them, two- and three-dimensional simplexes). And only those internal elements (diagonals and planes) are selected, that can implement the possible variant of polyhedration. If several versions of the polyhedration are possible as a result of the internal diagonals competition, the final decision should be confirmed by the experiment.

2.2. Formulas, connected the number of 0-, 1-, 2-, 3-dimension simplexes within the initial complex

The TCLSDD algorithm uses formulas, connected the number of the graph vertices (0D) and links between them (1D) with the number of 2D and 3D simplexes. If to represent the triangular prism of the quaternary reciprocal system A,B,C||X,Y with its stoichiometric compounds as a graph, then V (the number of graph Vertexes) and L (the number of Links between them) in the adjacency matrix are related by expressions [8]:

$$V = V_0 + V_E + V_F + VI$$ and $$L = L_E + L_F + L_I$$

where $$V_0 = 6$$ is the number of the prism vertices, $$V_E$$, $$V_F$$, $$V_I$$ are the number of binary, ternary, quaternary compounds, that are the points on Edges, Faces and Inside the polyhedron; $$L_E$$, $$L_F$$, $$L_I$$ are the number of Edges (simple binary subsystems without compounds) and diagonals (quasi-binary sections), on Faces and Internal diagonals, respectively.

L is equal to the number of unit elements of the adjacency matrix, $$V \bullet V$$ is the number of all elements of the square adjacency matrix, and $$(V^2-V)/2$$ is the number of all elements above (or below) of its main diagonal; therefore, L can be calculated as

$$L = \frac{(V^2-V)}{2} - L_0 + L_7,$$

where $$L_0$$ is the number of all zero elements of the adjacency matrix, and $$L_7$$ is the number of all links, unknown from the boundary elements. Each unknown element in the adjacency matrix can be labeled with the subscript "?". Further, all of these L_7 elements will take the value zero or unity, depending on whether or not the link corresponding to such element becomes a stable internal diagonal.

Because the triangular prism of the quaternary reciprocal system A,B,C||X,Y has $$L_E = 9$$ edges and $$S_E = 5$$ faces (two triangular and three quadrangular ones), the edges are divided by $$V_E$$ points into $$L_E = 9 + V_E$$ segments. The numbers $$L_E$$ of diagonals, $$S_E$$ of 2D Simplexes on Faces, $$S_I$$ of Internal secant planes, and T of 3D Tetrahedrons depend on the numbers $$V_E$$, $$V_F$$, $$V_I$$ of binary, ternary, quaternary compounds, respectively, and the number LI of internal diagonals [8]:

$$L_E = 3 + 2V_E + 3V_F, \quad S_E = 8 + 2V_E + 2V_F, \quad S_I = 2 + V_E + V_F + 2V_I + 2L_I, \quad T = 3 + V_E + V_F + V_I + L_4$$

There are known the formula of Euler $$V - L + S = 2$$ and Schlefi-Stringem $$V - L + S - T = 1$$, which links the number of simplexes of different dimensions: vertices and edges of the graph, 2D and 3D simplexes. Surely they are useful to verify the polyhedration. However, they are not sufficient, when you search the internal secants of the polyhedron. Because it is required to distinguish among the L and the S simplexes those ones, that belong to the faces of the original complex, and those, that are within the polyhedron. Similar, the simplexes S and T can be created either using the internal diagonals, or without them.
2.3. Polyhedration of systems with competition of internal diagonals

If to form the planes $x_i x_j x_k$ from unit elements of the adjacency matrix or segments $x_i x_j$ and from all its elements labeled with the subscript ",", these planes are divided into the following groups: $S_i$ planes on faces; $S_i^*$ internal planes formed without using internal diagonals; $S_i^{**}$ internal planes in which at least one of the sides is a possible internal diagonal and its corresponding element in the adjacency matrix is subscripted "*".

If the equality $S_i=S_i^*$ is valid, i.e., if the number of internal planes $S_i^*$, formed without internal diagonals, satisfy formulas (2) at $L_i=0$, then there can be the only variant of polyhedration without internal diagonals. Then all elements, which labeled as "?", are assigned zero.

If $S_i^*<2+V_i+V_i-2V_i$, then $L_i>0$, and missing internal planes should be taken from the sets of $S_i^{**}$ by selecting those satisfying formulas (2).

| Table 1. Prediction of internal planes ($S_i$) and tetrahedra ($T$) in the system with two binary compounds ($V_i=2$, $V_i=V_i=0$) (Matrix $R_1$), which belong to different ternary systems and to the same reciprocal ternary system, for two variants of polyhedration (Figure 1) |
|---------------------------------------------------------------|
| a) $S_i=2+V_i+V_i-2V_i+2L_i=2+2+0-0+2=6$ ($x_i x_j$ or $x_i x_j x_k$) |
| elements with "?" | with element $x_i x_j$ | with element $x_i x_j x_k$ |
| $x_1 x_2 x_3$, $x_3 x_2 x_4$ | $x_1 x_3 x_4$, $x_3 x_4 x_5$, $x_4 x_5 x_6$, $x_5 x_6 x_7$, $x_6 x_7 x_8$ |
| 2 | 4 |
| b) $T=3+V_i+V_i+V_i+L_i=3+2+0-0+1=6$ ($x_i x_j$ or $x_i x_j x_k$) |
| without elements with "?" | with element $x_i x_j x_k$ |
| $x_1 x_2 x_3 x_4$, $x_2 x_3 x_4 x_5$ | $x_1 x_2 x_3 x_4$, $x_1 x_2 x_3 x_4$, $x_2 x_3 x_4 x_5$, $x_2 x_3 x_4 x_5$ |
| 2 | 4 |

Thus, combinations of nonzero elements of the adjacency matrix, taken three at a time, give lists of all 2D simplices. From them according to formulas (1) and (2), groups of simplices are formed.

Suppose, for example, two binary compounds $x_i x_j$ and $x_i x_j x_k$ in the quaternary reciprocal system belong to the same ternary reciprocal system and to the different ternary systems (Figure 1, Table 1). The correspondent adjacency matrix

$$
R_1 = \begin{pmatrix}
|x_1| & |x_2| & |x_3| & |x_4| & |x_5| & |x_6| & |x_7| & |x_8|
\end{pmatrix}
$$

has two unknown elements $x_3 x_7$ and $x_3 x_7$. They are labeled as "?". If to write from $R_1$ all nonzero element combinations, taken by three, then we have got the list of triangles:

$X_1 X_2 X_3$, $X_1 X_3 X_4$, $X_1 X_4 X_5$, $X_1 X_5 X_6$, $X_1 X_6 X_7$, $X_1 X_7 X_8$, $X_2 X_3 X_4$, $X_2 X_4 X_5$, $X_2 X_5 X_6$, $X_2 X_6 X_7$, $X_2 X_7 X_8$, $X_3 X_4 X_5$, $X_3 X_5 X_6$, $X_3 X_6 X_7$, $X_3 X_7 X_8$, $X_4 X_5 X_6$, $X_4 X_6 X_7$, $X_4 X_7 X_8$, $X_5 X_6 X_7$, $X_5 X_7 X_8$, $X_6 X_7 X_8$, $X_7 X_8 X_9$.

Planes $X_1 X_2 X_3$ and $X_1 X_2 X_7$ must be deleted because links $X_1 X_4$ and $X_4 X_7$ are absent. Further $S_i=8+2V_i+2V_i=8+4+0=12$ simplices are deleted from the list, because they are belong to faces:

$X_1 X_3 X_7$, $X_2 X_3 X_7$, $X_4 X_5 X_8$, $X_3 X_6 X_7$, $X_1 X_3 X_6$, $X_1 X_4 X_6$, $X_1 X_5 X_7$, $X_1 X_7 X_8$, $X_2 X_3 X_7$, $X_3 X_7 X_8$, $X_4 X_5 X_6$. 

are two competitive elements of the expression b) and the rest internal planes are grouped (Table 1a): \( S_{1} = 2 - x_{1}x_{6}x_{8}, x_{1}x_{3}x_{7} \) - are formed by unit elements of the \( R_{1} \) matrix, \( S_{2} = 4 \) – one side of triangles \( x_{1}x_{3}x_{8}, x_{3}x_{5}x_{8}, x_{3}x_{6}x_{8}, x_{3}x_{7}x_{8} \) is a possible internal diagonal \( x_{1}x_{3}x_{8} \). There is another group (\( S_{2} \)) of four possible internal planes \( x_{1}x_{6}x_{7}, x_{1}x_{6}x_{7}, x_{5}x_{6}x_{7}, x_{6}x_{7}x_{8} \). They are formed by other unknown element of the \( R_{1} \) matrix \( x_{6}x_{7} \).

Figure 1. Polyhedration of the quaternary reciprocal system with two binary compounds \((x_{7}, x_{8} \) belong to different ternary systems and to the same reciprocal ternary systems) and the only one internal diagonal: \( x_{6}x_{7} \) (a) or \( x_{3}x_{8} \) (b).

Table 2. Prediction of internal planes (\( S_{1} \)) and tetrahedra (\( T \)) in the system with two binary compounds \((V_{b}=2, V_{r}=V_{m}=0) \) (Matrix \( R_{2} \)), which belong to different ternary and reciprocal ternary systems, for two variants of polyhedration (Figure 2)

a) \( S_{1} = 2 + V_{b} + V_{r} + 2L = 2+2+0+4=8 \) \((x_{1}x_{8}+x_{7}x_{8} \text{ or } x_{6}x_{7}+x_{7}x_{8})\)

| without elements with \( "?" \) | with element \( x_{2}x_{8} \) | with element \( x_{6}x_{7} \) | with element \( x_{7}x_{8} \) | with elements \( x_{2}x_{8}+x_{7}x_{8} \) | with elements \( x_{6}x_{7}+x_{7}x_{8} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( x_{1}x_{5}x_{8} \) | \( x_{2}x_{3}x_{8} \), \( x_{2}x_{5}x_{8}, x_{2}x_{6}x_{8} \) | \( x_{2}x_{6}x_{7}, x_{3}x_{6}x_{7}, x_{5}x_{6}x_{7} \) | \( x_{1}x_{7}x_{8}, x_{3}x_{7}x_{8}, x_{5}x_{7}x_{8} \) | \( x_{2}x_{7}x_{8} \) | \( x_{6}x_{7}x_{8} \) |
| 1 | 3 | 3 | 1 | 1 |

b) \( T = 3 + V_{b} + V_{r} + L = 3+2+0+2=7 \) \((x_{2}x_{8}+x_{7}x_{8} \text{ or } x_{6}x_{7}+x_{7}x_{8})\)

| without elements with \( "?" \) | with element \( x_{2}x_{8} \) | with element \( x_{6}x_{7} \) | with element \( x_{7}x_{8} \) | with elements \( x_{2}x_{8}+x_{7}x_{8} \) | with elements \( x_{6}x_{7}+x_{7}x_{8} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( x_{1}x_{4}x_{5}x_{8} \) | \( x_{2}x_{3}x_{6}x_{8}, x_{2}x_{5}x_{6}x_{8} \) | \( x_{2}x_{3}x_{6}x_{7}, x_{2}x_{5}x_{6}x_{7} \) | \( x_{1}x_{3}x_{7}x_{8}, x_{1}x_{5}x_{7}x_{8} \) | \( x_{2}x_{3}x_{7}x_{8} \) | \( x_{3}x_{6}x_{7}x_{8} \) |
| 1 | 2 | 2 | 2 | 2 |

Expression \( S_{1} = 2 + V_{b} + V_{r} + 2L = 2+2+0+4+2L \) satisfies to formulas (2), if \( S_{1} = S_{2} + S_{2} = 2+4=6 \), or if to take two planes \( S_{2} \) and one of two groups \( S_{2} \). As a result, there are two competitive elements of the \( R_{1} \) matrix \( x_{1}x_{8} \) (Figure 1a) and \( x_{6}x_{7} \) (Figure 1b). The final answer, which element receives the designation "1" - and the corresponding link become the internal diagonal, - and which receives the designation "0", will give the experiment. The list of tetrahedra is formed after analysis of the planes that were selected as possible internal ones (Table 1b).
If two binary compounds $x_7$ and $x_8$ belong to different ternary and ternary reciprocal systems (Figure 2, Table 2), and the $R_2$ matrix has three unknown elements,

\[
\begin{bmatrix}
  x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 & x_8 \\
  x_1 & 0 & 1 & 1 & 1 & 0 & 1 & 1 \\
  x_2 & * & 1 & 0 & 1 & 1 & 1 & ? \\
  x_3 & * & 0 & 0 & 1 & 1 & 1 & 1 \\
  x_4 & * & 1 & 0 & 0 & 1 & * & ? \\
  x_5 & * & 1 & 1 & 1 & * & ? & ? \\
  x_6 & * & ? & 1 & * & ? & * & ? \\
  x_7 & * & ? & ? & * & * & ? & ? \\
  x_8 & * & ? & ? & ? & ? & ? & ? 
\end{bmatrix}
\]

then selection of 21 nonzero elements (18 "1" and 3 "?") by three gives $S_f=8+2V_2+2V_3=8+6+0=14$ triangles on faces and 12 inside the prism (Table 2a). The only plane is formed without elements, labeled as "?". Three planes are formed with the help of one of unknown elements. And there are planes, formed by a pair of elements "?": $x_2x_8+x_7x_8$ or $x_6x_7+x_7x_8$.

\[\text{Figure 2. Polyhedration of quaternary reciprocal system with two binary compounds (}x_7, x_8\text{ belong to the different ternary and reciprocal ternary systems) and with the two internal diagonals: }x_2x_8+x_7x_8 \text{ (a) or }x_6x_7+x_7x_8 \text{ (b)}\]

Selection of planes in accordance to formulas (2) gives two alternative groups; every of them has 8 planes. The element $x_7x_8$ becomes the internal diagonal in any case, and the experiment is necessary only for one of two other diagonals.

As a result, we have the polyhedration method, which gives a possibility to control every stage of the process of dividing of the initial complex into simplexes and simultaneously to understand, which of possible internal secant elements (diagonals ans planes) are able to participate in polyhedration. The method helps not only to verify the polyhedration correctness, but to find all possible variants of polyhedration at competition of internal secant elements.
3. Results and Discussion

By the TCLSDD algorithm [6,7]:

1. in the Ba,Ca,K||F,WO₄ system with three binary compounds, the only variant of polyhedration was determined: with one internal diagonal CaF₂-K₂WO₄•BaWO₄;

2. in the Na,K,Ba||WO₄,F system with four binary compounds, two variants of polyhedration were found: with one of the competing internal diagonals, (NaF)₂-K₂WO₄•BaWO₄ or BaF₂-K₂WO₄•Na₂WO₄;

3. in the K,Na,Ca||Cl,NO₃ system with two binary compounds and one ternary compound, two variants of polyhedration were determined, with the stable internal diagonal (NaCl)₂-(KCl)₂•2Ca(NO₃)₂, and with one of the two competing internal diagonals, (NaCl)₂-2(KNO₃)₂•Ca(NO₃)₂ or (NaNO₃)₂-(KCl)₂•2Ca(NO₃)₂;

4. among eight quaternary reciprocal systems (Li,Sr,Na||Cl,NO₃, Ca,Na,K||F,MoO₄, K,Na,Li||Cl,NO₃, Ba,Ca,K||F,WO₄, Ba,Ca,K||F,MoO₄, Ba,Na,K||F,MoO₄, Na,K||Cl,NO₃,NO₂, Li,K,Ba||F,WO₄), the polyhedration of only three systems - Li,Sr,Na||Cl,NO₃, Ba,Ca,K||F,WO₄, Ba,Ca,K||F,MoO₄ - with participation of one internal diagonal was performed correctly [3,4]. In the polyhedration results for the other five systems the contradictions were detected.

4. Conclusion

The first variant of the TCLSDD algorithm, presented in [6], is possible to simplify, if to select according to formulas (2) the internal planes only (Table 1a and Table 2a). In this case the final result of polyhedration will be got automatically in the tetrahedral form (Table 1b and Table 2b). TCLSDD algorithm is a powerful tool to divide the multidimensional complex into the simplexes or more simple microcomplexes, and to enquire the contradictions in the published results of the multicomponent systems polyhedration.

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